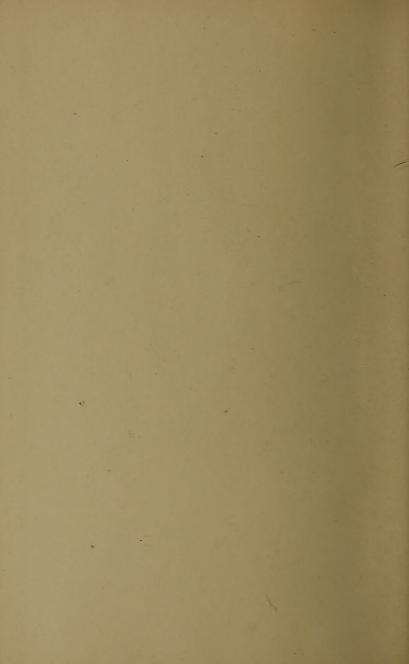
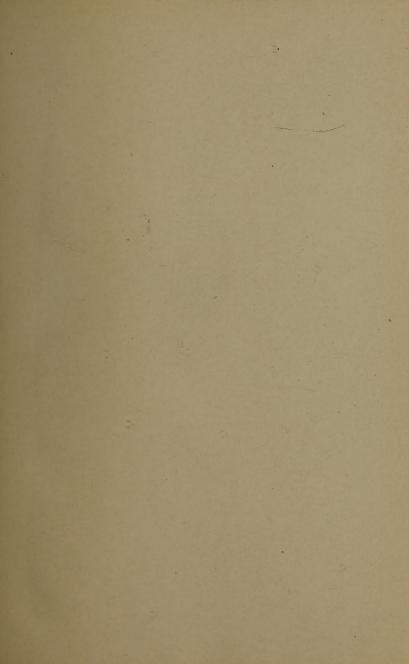
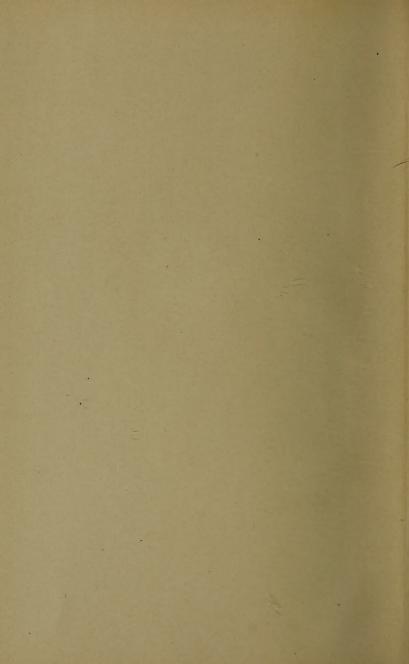
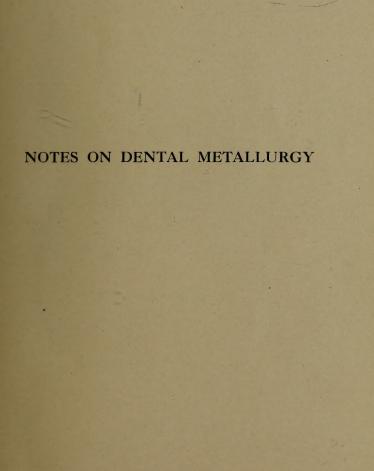


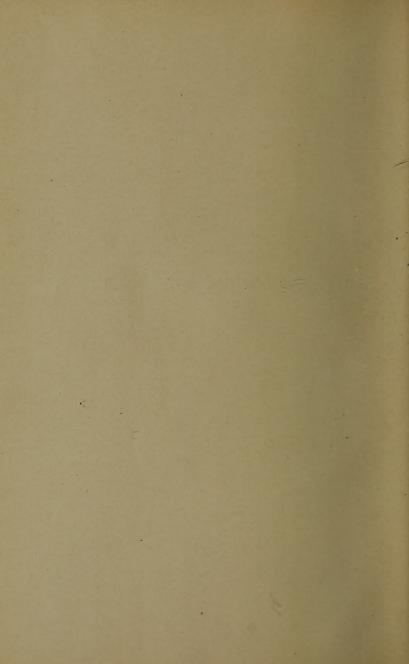
Wallace Seccombe











# NOTES ON DENTAL METALLURGY

# FOR THE USE OF DENTAL STUDENTS AND PRACTITIONERS

BY

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## PREFACE TO SECOND EDITION

In presenting the second edition of this book of notes I desire to take the opportunity of thanking the profession, practitioners, and students, for the very cordial reception granted the first edition. Also to those lecturers in Britain and abroad who have from time to time favoured me with their views and valuable advice towards the improvement of the book.

In this edition much of the text has had to be rewritten to bring it into line with the subject as it is to-day. The chapter on Alloys, beginning with their Constitution, has been written by Professor A. Campion, of the Royal Technical College, Glasgow. The subject of alloys is occupying so important a place in our present-day literature that I approached him to undertake the task of condensing the subject to the requirements of such a notebook as this.

The chapter on Dental Amalgams has been entirely rewritten. In dealing with such a thorny subject it is almost impossible to avoid running counter to views held and expressed by individual lecturers and teachers, and I have kept as closely as is permissible to the average opinion expressed in textbooks, magazine articles, etc., culled from my study of these and from my practical work done.

The student would be well advised in studying dental

metallurgy for examination purposes to avoid attempting to get up the subject in minute detail, as the underlying principals are the essentials, and are emphasized in examinations.

I hope the addition of many useful alloys not included in the previous edition, and several other features, will assure this edition an equally kindly reception by the practitioners and students.

My thanks are to be expressed to Professor Campion for checking the entire text for metallurgy, and to Dr. H. McKay for the dental aspect of the subject.

WALTER BRUCE HEPBURN.

The Glasgow (Incorporated) Dental Hospital and School, May, 1915

## PREFACE TO FIRST EDITION

This book of notes has been compiled for the use of dental students preparing for the British, Colonial, and American dental degrees, the various college and school requirements having been consulted, and the necessary matter supplied, so far as these requirements come within the scope of metallurgy proper. Obsolete theories regarding the composition and behaviour of amalgams have been avoided, and only the opinions of the most authoritative have been included.

In the text the attempt has been made to describe only those processes for extraction of metals which are at present employed, obsolete processes being omitted, unless where brief reference to these assists in the understanding of present-day methods. The chapters dealing with pyrometry, casting of metals, testing of amalgams for their physical properties, are inserted to meet special college requirements; while that dealing with the behaviour of metals in the mouth is intended to direct the attention to what might be termed "applied metallurgy," an aspect of the subject which the writer considers has been neglected.

The book should appeal to the general dental practitioner, presenting as it does the subject in a condensed fashion, and furnishing him in the text and Appendix with the composition of many useful and valuable alloys and solders.

No claim of originality is made for any matter con-

tained in the text. Acknowledgment is made where a direct reference can be traced; and should such be omitted in any instance, the writer would proffer his humblest apologies.

Where different opinions are held, he has attempted to avoid theories in favour of practice, especially where the practical experience has been gained after years of observations. In this way he hopes to have presented the subject as it is, and to guard the student from imbibing theories in mistake for practice.

He has to acknowledge with thanks the valuable assistance rendered him by Dr. H. Mackay, L.R.C.P. and S. (Edin.), L.F.P.S., L.D.S. (Glasg.), Examiner on Dental Metallurgy to the Royal Faculty of Physicians and Surgeons, Glasgow. He is also greatly indebted to Professor A. Campion, Lecturer on Metallurgy to the Glasgow and West of Scotland Technical College, for correcting the proofs; to Sydney Smith, Esq., M.A., for general corrections in the text; and to Messrs. C. Ash and Sons, the Dental Manufacturing Company, and others, for their kindly assistance in answering all questions addressed to them; and he wishes to take this opportunity of expressing his thanks to hem.

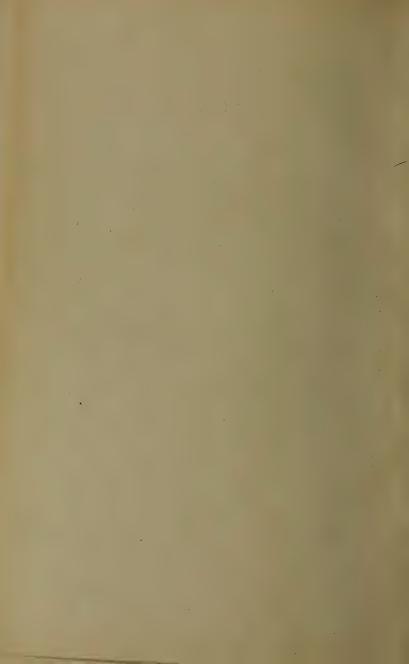
WALTER BRUCE HEPBURN.

THE GLASGOW (INCORPORATED) DENTAL HOSPITAL AND SCHOOL,

November, 1910.

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# NOTES ON DENTAL METALLURGY

#### CHAPTER I

#### PHYSICAL PROPERTIES OF METALS

METALS as a class may be said to possess certain generic properties which distinguish them from the non-metallic elements.

Thus, they may be regarded as possessing, in varying degrees, the properties of malleability, ductility, elasticity, tenacity, conductivity, weldability, toughness, density, specific heat, crystallization, odour and taste, galvanic action, hardness, occlusion of gases, lustre, fracture, sonorousness, diffusibility, volatility, and flow. At ordinary temperatures metals are solid, with the exception of mercury, which is liquid at ordinary temperatures, and solid at  $-39^{\circ}$  C. They are all fusible; in mass they are opaque; they are diffusible on melting, and may be alloyed.

**Malleability** is the property of being permanently extended in all directions without rupture, either by pressure or hammering.

Gold is the most malleable of all the metals, and has been laminated into foil of such extreme thinness as  $\frac{1}{282000}$  inch. Malleability is greatly affected by the degree of purity of the metal; the purer the metal, as a rule, the greater the malleability. (See Alloying.) It is

also affected by the temperature at which the metal is worked, some metals fracturing if rolled when cold, others exhibiting the opposite tendency. Zinc, for example, fractures if rolled when cold or at a red heat, but is readily reduced in thickness if rolled at 150° C.

Metals which cannot be rolled or worked when cold or at a low temperature are said to be "cold short."

Metals which tear or crack when rolled or treated mechanically at a red heat are said to be "red short."

Malleability is greatly increased by annealing. The operation of annealing usually consists in heating the metal to a more or less high temperature and allowing to cool comparatively slowly. The exact temperature of heating and mode of cooling varies according to the nature of the metal. Annealing processes are dealt with more fully under the treatment of the individual metals.

Annealing causes a rearrangement of the crystalline structure of the metals, enabling them to be rolled, hammered, or otherwise mechanically treated without

tearing.

Relative degrees of malleability are determined by hammering or rolling the metal when in the cold state, and registering the reduction of thickness which can be produced without annealing.

The following are in order of malleability by rolling: Gold, silver, aluminium, copper, tin, lead, platinum, zinc iron, and nickel.

By hammering (malleability proper): Lead, tin, gold, zinc, silver, aluminium, copper, iron, platinum, and nickel.

**Duetility** is the property of being permanently elongated by a tensile force, or of being drawn into wire, and is possessed by most malleable metals in varying degrees.

Purity of the metal influences ductility generally, although alloying in many instances increases ductility. While this is true generally, tenacity affects ductility more than malleability. Heat effects ductility, which generally decreases as the temperature is raised, but a

regular ratio does not exist between ductility and temperature. Iron, for instance, is less ductile at 100° C., and more ductile at 200° C., than when at 0° C. Copper gradually decreases in ductility with rise of temperature to about 730° C., when it shows a sudden and remarkable increase, the ductility between 730° C. and 800° C. being about twice as great as at ordinary temperature. Above 800° C. the ductility rapidly decreases. The ductility of aluminium increases with temperature to 600° C., and then very abruptly falls. The ductility is effected by the rate at which the tensile force is applied, and also by thermal and mechanical treatment; gold, platinum, and silver, for example, requiring frequent annealing and drawing at very moderate speed.

The following are in order of ductility: Gold, silver,

platinum, iron, nickel, copper, aluminium, zinc.

• Elasticity is the extent to which a metal may be elongated by tension, without remaining permanently extended on the removal of the stress which caused the

elongation.

The point at which the elasticity and the stress applied exactly counterbalance each other is referred to as the "limit of elasticity"—that is to say, the point which the metal has reached when a greater stress would cause the shape of the metal to be permanently altered. Such alteration, when it does occur, is referred to as the "permanent set," and the point at which it occurs is termed the "yield point."

Experiments have gone to show that metals are increased in rigidity if strained just beyond their limit of elasticity. The elasticity of a metal is powerfully influenced by the presence of impurities, and by methods of straining, annealing, and alloying. The temperature at the time of application of the stress greatly affects

the elasticity.

**Tenacity** is the property of resisting fracture when subjected to a tensile or stretching force.

This property in a metal is also affected by the presence of impurities, thermal treatment and alloying. Gold is greatly affected by even traces of such metals as lead, bismuth, and antimony, losing its ductility and malleability, and being changed into a brittle and unworkable condition. (See Properties of Gold.)

Phosphorus has a marked effect if present in malleable iron. Karsten states that 0.3 per cent., while not sensibly affecting the tenacity, increases the hardness; while 0.5 per cent. diminishes the tenacity, and the

metal shows signs of deterioration.\*

As tested for relative tenacity, the metals occur in the following order: Steel, iron, copper, platinum, silver, gold, zinc, tin, and lead.

**Conductivity** is the power possessed by a metal to conduct heat and electricity.

Metals as a class are regarded as the best conductors, and, as with the other properties, the conductivity may be powerfully influenced by the presence of impurities. Thus, copper for electrical purposes must be as pure as possible, as any trace of silver (the metal with which it most frequently occurs) reduces this power very considerably. Silver and copper, when pure, rank highest amongst the metals for the property of conductivity, vet if alloyed, or present in each other in even small traces, the property is much reduced. Temperature plays an important part in the conductivity of metals. If the temperature is raised, the conductivity decreases; if it is lowered, the conductivity increases. As zero is approached, the conductivity of metals becomes more uniform. The metals are arranged in their relative powers of conductivity as follows, silver in the pure state being taken as the highest, and representing 100: Silver, 100; copper, 73.6; gold, 53.2; tin, 15.2; iron, II.9; steel, II.6; lead, 8.5; platinum, 8.4; German or nickel silver, 6.3.

<sup>\*</sup> Greenwood.

**Weldability** is the property possessed by most metals of being joined by pressure or hammering without the aid of solder.

This property is possessed to a remarkable extent by platinum, gold, and iron. Platinum is welded from the finely divided deposited form into sheets, bars, etc., heat being unnecessary (see Platinum Reduction); so also is gold, as employed for filling purposes, in matte, cubes, foils, etc. Heat is generally essential to effect complete union or cohesion of the metals. For iron as malleable iron, or for soft steel as treated industrially, heat is employed, and clean surfaces of the metal brought together, the union being then effected either by hammering or rolling.

In recent years the term "weld" has been applied to indicate a union of metals by fusion, either of the metal to be joined, or of a separate piece of metal used in the same manner as solder. The process is obviously an "autogenous soldering," although commonly termed

"autogenous welding."

An ideal weld should exhibit not only perfect union of the pieces of metal, but the metal in the welded region should be in the same condition as that of the original metal.

A gold filling perfectly inserted should not show any tendency to disintegrate, and under the microscope should show a homogeneous structure. The term "cohesive," as especially employed in dental literature to gold, refers to this property only, which is possessed by the metal to such a remarkable degree.

**Toughness** is the power possessed by a metal of resisting fracture by bending or rolling. Or, "the property of resisting separation of the molecules after the limit of elasticity has been passed."\*

**Hardness** is a property possessed in varying degrees by all metals, and is the resistance offered by the mole-

<sup>\*</sup> Sir W. Roberts-Austin.

cules of a substance to separation by the penetration of another body.

**Density, or Specific Gravity.**—As a rule the specific gravity of the metals is recorded when they are in the pure and cast condition, as any process which will tend to bring the molecules into more intimate contact, such as hammering or rolling, will increase the specific gravity. Zinc when freshly cast is highly crystalline, and has a specific gravity of 6.68, whereas on being rolled this is increased to 7.2. Annealing, again, will reduce the density.

**Specific Heat.**—Metals, like other bodies, have their specific heat, and to measure the relative specific heats, the amount of heat necessary to raise water from o° C. to 1° C. is taken as the unit. Lowering the temperature of the metal generally decreases the specific heat.

**Crystallization.**—All metals are said to be capable of crystallization, by which is meant that the molecules arrange themselves in a certain geometric order in the process of the metal cooling from a gaseous or liquid state to the solid. While few metals are found native in the crystalline form, many of them may be deposited as crystals by passing a current of electricity of low intensity through a solution of the metal, or by fusion followed by slow cooling. Gold in the matt and crystalline forms are good examples of this property. (See Filling Golds.) Metals in the cast state frequently exhibit very perfect crystalline forms, which forms are influenced by the manner of casting, the rate of cooling, and the temperature at which the metal is poured. This property is more fully dealt with under the separate metals.

Odour and Taste.—Metals are said to possess characteristic odours and tastes. Arsenic, for example, when heated, evolves a garlic odour, and to the tongue has a sweetish taste. Zinc also has a characteristic odour when burned or excessively heated, the metal, on being reduced to the oxide, burning with a bright flame, and

giving off the white flocculent oxide. Alloys, as used for filling purposes, possess odours which become more pronounced when the alloys are amalgamated with mercury. The most common odour resembles a sulphide, but varies even in separate mixings of the same alloy. The late Professor Essig attributed this odour to a voltaic action set up between the metals on the addition of the mercury, but this theory must be accepted with many reservations.

Galvanic Action.—From a dental standpoint, the galvanic action between metals assumes much importance, when we consider the metals employed as filling materials. The action is generally most pronounced in mouths where the saliva is acid to litmus-paper, and where two fillings of different compositions are brought into contact, or are in fairly close proximity, the saliva in this case completing the circuit. Gold and amalgam fillings, and gold and dental alloy dentures, are common sources of this trouble, the pulps of the teeth responding to the galvanic action between the metals. In such cases, where gold and amalgam fillings are at fault, the filling should be either in gold or in amalgam, or the pulp protected by a coating of oxyphosphate of zinc cement, which acts as a non-conductor. mouths it is frequently observed that the fillings are corroded or washed out, especially towards the cervical margins, which may be attributed to the solvent action of the saliva and the current generated. (See chapter on Behaviour of Metals in the Mouth.)

Occlusion and Diffusion of Gases.—Some metals have the power of dissolving gases; others are sufficiently permeable for the penetration of gases, whilst others again actually combine with gases to form chemical compounds, such as hydrides and nitrides. The recent researches of Sievert and associates (*Tt. Phys. Chem.*, 1907, lx. 129; 1909, lxviii. 115) cover practically the whole ground. They found that nitrogen and hydrogen

are not dissolved by cadmium, zinc, lead, bismuth, tin, antimony, aluminium, silver, or gold; that nitrogen is insoluble in copper, nickel, and palladium; and that neither carbonic oxide nor carbonic anhydride are dissolved by copper. It has been shown that under certain conditions hydrogen is soluble in palladium, nickel, iron, cobalt, and copper; nitrogen is soluble in iron, oxygen in silver, and sulphurous anhydride in copper. solubility of hydrogen and sulphurous anhydride in the solid metals is proportional to the temperature, but at each melting-point there is a break, when solubility increases with rise of temperature more rapidly than in the solid metal. The solubility of oxygen in silver at ordinary temperature is zero; it reaches its maximum at the melting-point, and decreases gradually with the rise in temperature of the liquid metal. Precipitated platinum and platinum metals readily absorb oxygen, hydrogen, carbon dioxide, and water, which, if driven off by heat, are not reabsorbed.

Sievert has also shown that hydrogen very readily diffuses through iron, platinum, copper, nickel and palladium, as does oxygen through silver above 770° C., and that hydrogen does not penetrate aluminium and silver, and that carbonic oxide does not diffuse through copper, iron, and nickel, nor does sulphurous anhydride through copper. In general, the diffusing power increases with the temperature; it is usually paralleled by the dissolving power, the leading exception being platinum, through which hydrogen diffuses at a low temperature, but by which it is not dissolved.

**Lustre.**—Lustre has long been regarded as characteristic of metals, and is due to the high degree of opacity possessed by them, the light on this account being reflected from their surface.

**Fracture.**—The fractures of metals are described as crystalline, granular, fibrous, columnar, or conchoidal. The nature and purity of the metal, the method of frac-

ture, and the rate of solidification and cooling, influence the character of the fracture. Sudden cooling generally prevents the formation of crystals, while slow cooling assists it.

**Sonorousness** of metals is well known, the clear note of a bell of silver, the resonance of steel wire in a piano, being common examples. The sonorousness of copper and gold is increased by alloying, "bell metal," for instance, being an alloy of copper and tin. Aluminium possesses it to a less extent, but is influenced very considerably by the method of casting.\* (See Aluminium.)

Flow of Metals.—Metals are capable of behaving, under suitable conditions, in the same manner as liquids; thus, from the solid state they pass into the liquid, then into the gaseous, and by cooling can be brought back to the solid. They are diffusible, and under pressure yield before it, this property being referred to as the "flow of metals" even when the metals are in the cold or solid condition. Professor Springs has demonstrated that metals, when subjected to pressure, behave in a manner closely resembling liquids. By means of a suitable press, the metal lead was made to flow into all the crevices of the press, and was found to have penetrated the less compact structure of the metal composing the press.† (See Preparation of Alloys by Compression.)

Diffusibility of Metals.—This property varies greatly with the different metals. Some diffuse with great freedom, while others remain as mixtures, and constantly disclose a tendency to separate or liquate on being remelted and allowed to cool. Advantage is taken of this property in manufacturing alloys or compounds of metals, which, if not disclosing an affinity for one another, will at least remain diffused sufficiently long for the purpose intended. Copper diffuses itself through gold with great freedom, so much so that 1,000 ounces

<sup>\*</sup> Faraday. † Sir W. Roberts-Austin.

of gold and 100 ounces of copper alloyed show on analysis a variation not greater than  $\frac{1}{1000}$ th part between the alloy first poured and the last. (See Alloys.)

Metals differ widely in their behaviour under the influence of heat. Tin and lead fuse below the point of redness; gold, silver, and copper, at higher temperatures; while platinum, iridium, osmium, etc., are infusible in ordinary furnaces, requiring the use of the oxyhydrogen blowpipe.

**Volatility** is the property of being converted into a state of vapour by the application of heat, and is possessed by most of the metals. Zinc, cadmium, arsenic, and mercury, are very volatile, arsenic passing into the gaseous state without becoming liquid. Advantage is taken of this property in separating highly volatile metals from their ores, such as mercury, zinc, etc.

Magnetic Properties of Metals.—Metals differ widely in their behaviour when placed in a magnetic field, and may be classed as paramagnetic or diamagnetic. A paramagnetic metal assumes a direction parallel to the magnetizing force. A diamagnetic metal assumes a direction at right angles to the magnetizing force.

Paramagnetic metals: Iron, nickel, cobalt, platinum, palladium, and osmium.

Diamagnetic metals: Silver, gold, copper, tin, zinc, mercury, cadmium, and lead.

Alloying affects the magnetic properties of metals; copper, for instance, a diamagnetic metal, if alloyed with even a small quantity of iron, becomes paramagnetic. Heat and the presence of impurities also affect this property. Metals differ widely as to the length of time they will retain the magnetism imparted to them; thus, while it is more difficult to induce hard-tempered steel to accept magnetism than soft iron or soft steel, it retains the induced magnetism much longer than either of the latter.

#### CHAPTER II

#### TERMS USED IN METALLURGY

**Ore.**—Applied to the minerals as they occur in the crude state, from which the metals are extracted. The ore is washed at the mines to free it from as much extraneous matter as possible, and the metallurgical interest in it begins. Only such minerals as contain metals in quantities or forms as to enable them to be extracted profitably are called ores.

Ores may contain metals—

In the native or metallic state—e.g., gold, silver, copper, mercury, and platinum.

As oxides—e.g., oxides of iron and tin.

As oxides combined with water—e.g., brown hæmatite or limonite.

Combined with sulphur, arsenic, antimony—e.g., lead sulphide.

Combined with halogens—e.g., silver chloride.

As acid salts—e.g., lead sulphate.

In a state of mixture or combination of the same metal.

As a combination of various metals and various compounds of these metals.

Metals are divided roughly into two divisions—i.e., noble and base metals.

**Noble Metals** are those which are readily separated from combinations with oxygen on being heated to redness.

Base Metals are those which do not readily yield their combination with oxygen by the aid of heat only.

Gangue, Matrix, or Vein-Stuff.—Applied to the refuse or extraneous earthy matter generally associated with ores.

Smelting.—Applied to the process or series of processes in which, by fusion, a metal or metallic compound is separated from its ores.

Flux.—Applied to the materials which are added to the ores to facilitate the reduction, or to combine with extraneous matter to form fusible compounds, which, as the metal is reduced, rise to the surface and may be drawn off, removing much of the impurities present in the form of a fusible slag. In much the same manner as borax is employed in soldering, to keep the surface to be soldered free from a layer of oxides or other impurities, which would hinder union of the surfaces by the solder.

Slag.—Applied to the compound of flux and extraneous matter separated from the metallic ores during the process of smelting.

Matte.—Applied to describe arsenides, antimonides,

and sulphides of metals.

Regulus.—Applied frequently to the sulphide formed when ores of iron, silver, or copper, are smelted with substances containing sulphur.

Speiss.—Applied to the arsenide of a metal.

Distillation.—Applied when a volatile metal is converted into a vapour, and subsequently collected by condensation—e.g., zinc.

Calcination.—Applied to the processes for expelling carbonic acid, water, and other volatile constituents, by

heat.

Roasting.—Applied to processes for heating ores and compounds in an oxidizing atmosphere.

Desiccation.—Applied to the drying process certain

ores are subjected to previous to reduction.

Dissociation.—Applied to the splitting up of chemical compounds by heat, electricity, or other measures, into

the composing elements. Most strictly applied to such

as are capable of being re-formed.

Cementation.—Employed to describe the diffusion of solids, such as carbon into iron (cementation process), also the recovery of silver from solid gold, the term "cementation" being derived from the cement or compound employed for this purpose.\*

Liquation.—Applied to the process employed to separate two metals whose melting-points are widely different, the more fusible metal separating when its melting-point is reached. Also employed to denote the tendency, in many alloys, for the metals comprising the alloys to separate and arrange themselves according to their specific gravities.

Eliquation.—Applied to the process which consists in alloying a metal with three or four times its weight of lead (especially silver), casting it into round discs, and then applying moderate heat; the lead fuses, carrying most of the silver with it. (See Lead and Silver.)

Lixiviation.—The process of washing or leaching, employed to separate certain soluble compounds in ores from impurities or insoluble residues.

Scorification and Cupellation.—Described under Gold

and Silver.

Sublimation.—Almost analogous to distillation, except that the metal is separated as a vapour and condensed to the solid—e.g., mercury.

Dry Process.—Applied to the series of processes in which heat is employed to extract metals from their ores.

Wet Process.—Applied to the series of processes in which the metals are extracted by means of solvents, such as ordinary acids, and the metals then deposited by means of electricity or other reagent from the solution.

<sup>\*</sup> Sir W. Roberts-Austin.

#### CHAPTER III

#### COMBINATION OF METALS AND NON-METALLIC ELEMENTS

METALS combine with certain non-metallic elements to form new classes of bodies. These are—

Chlorides.—All metals combine with chlorine to form metallic chlorides. The same metals may combine with chlorine in different proportions; we may have, for example, stannous and stannic chlorides, mercurous and mercuric chlorides. These chlorides are formed—

I. By bringing a current of chlorine gas into contact with the metal when strongly heated, or when in the form of the oxide, as detailed under the chlorination process for extraction of silver.

2. By acting upon the metals with hydrochloric acid.

3. By dissolving a metallic oxide, hydroxide, or carbonate, in hydrochloric acid.

4. By substituting one metal for another, as with

mercuric chloride and tin.

5. By acting upon certain metals, such as gold, with aqua regia.

**Bromides.**—Metals combine with bromine to form metallic bromides only with less readiness than with chlorine.

**Iodides.**—Metals combine to form iodides, with properties closely resembling chlorides and bromides.

Sulphides.—Metals combine with sulphur to form sulphides. Many of the metals occur in the ores com-

bined with sulphur as natural sulphides, such as iron pyrites, zinc-blende, and galena. Some metals exhibit a natural affinity for sulphur; advantage is taken of this property in the reduction of metals from their ores, iron in several instances being added to the ore so that it may combine with the sulphur, for which it exhibits a strong affinity. Metallic sulphides may be artificially prepared by passing sulphuretted hydrogen through a solution of a metal, also by heating a metal in presence of sulphur, the metal being coated with a superficial layer of sulphide. This action is well marked with inferior grades of dental alloy, and in silver amalgam fillings the excess of silver induces the formation of a superficial layer of silver sulphide. Metallic sulphides are mostly insoluble in water, are solid at ordinary temperatures, and most of them fuse at a red heat.

Oxides.—Many metals are oxidized by exposure to air, moisture, or carbon dioxide; iron, for example, soon becomes coated with rust. Others, such as lead and zinc, are converted to their oxides if heated beyond their melting-points. Oxides may be formed artificially by treating some metals with nitric acid, and from hydrated oxides by the application of heat. The metallic oxides assume their greatest importance in reduction processes, in which the object is to convert a metallic sulphide, arsenide, etc., into an oxide, from which the metal is reduced to the metallic state. They are also used for purifying the raw metal during refining. (For metallic oxides, see especially Lead and its Reduction.)

**Fluorides.**—These compounds are formed by heating certain metals or metallic oxides in hydrofluoric acid. As a class they are easily fused, and their properties closely resemble those of metallic chlorides and bromides.

#### Fluxes.

Those metallurgical agents known as "fluxes" are employed to assist in the separation of foreign or extraneous substances combined with an ore, by combining with them to form a slag, thus allowing the metal to melt free. For general purposes the following are the

chief fluxes employed:

I. Lime is used largely in iron-smelting, as it acts as a powerful base for removing silica. Dolomite, the carbonate of lime and magnesia, is largely made use of, especially as a constituent of furnace linings. (See Bessemer Process for steel.)

2. Barytes has a similar action, and is of use especi-

ally in the concentration of nickel speiss.

3. Siliceous materials, such as siliceous slags from other furnace charges, quartz, and natural silicates, are employed where ores containing an excess of basic materials have to be reduced.

4. Metallic oxides are used as fluxes, as instance the addition of hammer scale or iron oxide in lead-smelting.

5. Borax is used in cleaning and soldering gold and the precious metals.

6. Common salt is added to the furnace charge in

treating dental workroom lemel or sweep.

7. The liquid soldering fluid much used by goldsmiths and jewellers contains a saturated solution of equal parts of borax and boric acid. The liquid flows into crevices and small spaces much better than ground borax and water, and induces the solder to flow.

8. Parr's fluxed wax mixed with borax. The wax, as it is burned out, carries the borax to the crevices to be soldered. There is also a preparation of gold solder and flux combined as a powder, especially useful in soldering in bridge or continuous gum work.

soldering in bridge or continuous gum work.

There are several other agents employed, especially in the treatment of scrap gold and brittle gold, such as potassium nitrate, ammonium chloride, paraffin wax as used to prevent oxidation during soldering of aluminium, etc.

#### CHAPTER IV

#### MERCURY

Atomic weight, 200. Symbol, Hg. Melting-point, - 39° C. Specific gravity, 13.59.

Occurrence.—Cinnabar, the red sulphide of mercury (HgS), is the chief source of the metal, and is often mixed with the free metal. Mercury also occurs native in small quantities, as a protochloride or native calomel, as the iodide and chloride in native amalgams of silver and gold, and also in several fahlores.

Preparation.—Mercury is generally prepared by dry methods of distillation, the wet methods and the electrolytic never having found much favour commercially. The dry methods may be divided into two groups:

I. Those in which the mercury is extracted by heating

the cinnabar in air.

2. Those in which the mercury is extracted by heating cinnabar with lime or iron, the air being excluded.

Of these, the first is most largely, if not almost ex-

clusively, employed.

By heating Cinnabar in Air.—This process consists in heating cinnabar in a shaft or reverberatory furnace with an excess of air to a temperature sufficiently high to cause the oxygen of the air to combine with the sulphur in the cinnabar to form sulphur dioxide, the mercury separating out in metallic form. The following formula explains the action:

$$HgS + O_2 = SO_2 + Hg.$$

The Iridian Process.—In this process the furnace consists of a shaft crossed by several perforated arches, on which the crude ore is placed—the largest pieces on the lowest arch, the smaller pieces on the higher, and the unreduced ore from previous furnace charges, as a powder on the top arch. This powder is mixed with water and clay, and shaped into blocks. When the fire is kindled on the floor of the shaft, the heated products of combustion rise, the air combining with sulphur dioxide, at the same time liberating traces of sulphuric acid. As the heat increases the mercury distils over, and condenses as it comes in contact with the air of the condensing chambers, placed to right and left of the central shaft. Most of the mercury is collected from the condensers nearest the furnace, the others containing some mercury mixed with heavy dust. In some instances inclined plains are inserted in the last chamber of the series, over which water is caused to flow, so keeping the air as cool as possible, and preventing uncondensed mercury from escaping.

Reduction with Iron, Lime, etc.—There are several of these processes, the essential features of which consist in charging the cinnabar, mixed with iron or lime, into closed vessels. The mercury distils, and is drawn through pipes let into the base of the vessels, which are either immersed in water or kept cool by water circulating round them. The use of lime is said to yield better results. The action may be expressed thus:

 $_{4}$ HgS+ $_{4}$ CaO= $_{3}$ CaS+ $_{4}$ CaSO<sub>4</sub>+ $_{4}$ Hg.

Purification of Mercury.—The mercury as produced by these processes generally contains traces of the metals contained in the ores, such volatile metals as zinc, antimony, and bismuth, having passed over with the mercury; while tin and antimony, being soluble in mercury, are dissolved as they pass over with it. In the various methods of extracting the mercury by the dry processes, no special precautions are taken to prevent

the volatilizing and solution of these metals, as it would be difficult to keep the furnace at a heat sufficient to distil the mercury alone. As some of these metals are worth recovering, however, the temperature is raised with the purpose of volatilizing them, and they are recovered from the liquid mercury. The following methods are employed:

I. Impurities not soluble in mercury are removed by passing the mercury through chamois leather, when

they are left adhering to the skin.

2. Redistilling at a low temperature, when the mercury

alone passes over.

3. Lead, bismuth, and zinc, are removed by washing the mercury in dilute nitric acid. The metals are converted to nitrates, together with a small proportion of the mercury.

4. Pronitrate of mercury may be used instead of nitric acid, the base metals displacing the mercury in the pronitrate, which, thus liberated, combines with the mercury on being purified.

5. Chemically pure mercury is obtained by redistilling the metal in vacuo after treatment by sulphuric acid

containing mercurous nitrate.

6. Electrically Pure Mercury.—In these processes commercial mercury is the anode, and carbon rods the cathodes. The bath or electrolyte contains 17 per cent. nitric acid and 4 per cent. potassium nitrate. The current is never permitted to rise above 0.75 volt, and the metals, such as zinc, cadmium, bismuth, lead, tin, etc., pass into solution, leaving the mercury pure.\*

**Properties of Mercury.**—Pure mercury always presents a bright clear surface, and if poured slowly from a shallow vessel or over a flat surface runs with a clear and sharply defined edge. The presence of ordinary commercial impurities may be detected by the dull surface of the mercury; by the appearance of fine dust

<sup>\*</sup> Smith's "Dental Metallurgy," p. 128.

or grit on the surface if the mercury is shaken; and by the formation of a long-drawn-out ending or tail if it be poured or made to run slowly over a level surface, such as a hand-mirror. For dental purposes, such as the amalgamating of the alloys for fillings, electrically pure mercury is used, since the presence of such base metals as are either present as impurities or added as adulterations would injure the composition and properties of the amalgams.

Mercury possesses the singular property of being liquid at ordinary temperatures, and having a melting-point of -30° C. Below this temperature the metal becomes solid, contracting considerably on solidifying. In the solid state the specific gravity is increased by almost 6.50, owing to the contraction of the metal, and the consequent drawing of the molecules closer together. When solid, the metal is white, ductile, malleable, and crystalline. It boils at 360° C., forming a colourless vapour. When heated to about 270° C., it combines with oxygen to form mercuric oxide. The oxide is again decomposed into oxygen or metallic mercury. Mercury readily combines with gold, silver, platinum, bismuth, tin, zinc, and cadmium; with copper and iron less readily, unless the metals are previously brought to a fine state of division.

Combined with another metal, mercury forms an amalgam, and, as gold and silver are readily soluble in mercury, advantage is taken of this property in the extraction of these metals. (See Gold and Silver.)

Mercury and Tin.—The action of mercury on other metals is readily seen if an ingot of tin be immersed in mercury. In less than one minute the ingot will be rendered friable, and if allowed to remain longer will be completely dissolved.

Silvering of Mirrors.—In the process known as the "silvering of mirrors," an amalgam of tin and mercury is employed. The glass to be silvered is made perfectly free of scratches, and cleaned with putty powder.

Tin-foil is spread on a flat surface, rubbed free of creases, and covered over with a thin film of mercury. The glass is laid on, and pressure applied to bring its surface into perfect contact with the amalgam and to express air. The pressure is maintained for twenty-four hours. The table on which the glass is laid is tilted gradually at intervals to allow the excess of mercury to be run off, until the glass is in the upright position. The silvering is allowed several days to harden, and then covered with a lead paint to protect it.

Mercury and Silver.—Silver combines readily with mercury, and when they are combined in certain proportions the union of the metals is accompanied by the

evolution of heat.

Mercury and Gold.—Gold and mercury will readily combine, but the amalgam is friable and never used. Tin, gold, and silver as cylinders are employed to remove excess mercury from the surface of amalgam fillings. Care should always be taken to prevent mercury from coming in contact with gold fillings, crowns, plates, etc., as the mercury penetrates the gold, and in the case of fillings causes the surface to discolour, flake, and, if absorbed in excess, to break up. Crowns are badly discoloured by mercury, and, where the mercury is in excess, are acted upon rapidly by attrition during mastication.

Mercury and Copper.—The amalgam formed by the alloying of these metals, known as "copper" or "Sullivan" amalgam, is the only instance in which mercury is alloyed with another single metal for dental purposes.

(See Copper.)

Mercury and Platinum. — Mercury combines less rapidly with platinum than with gold, and the metals

are never employed together as an amalgam.

Mercury and Palladium.—The metals combine readily, the amalgam showing expansion when set. In the mouth the amalgam becomes almost jet black, the darkness being transmitted to the tooth structure. The

amalgam is never employed as a filling material. (See Palladium.)

Mercury and Bismuth, Cadmium, Antimony, or Lead.—Mercury combines with these more or less readily. It is added also as a constituent of some fusible metals to lower the melting-points.

Mercury and Nickel.—The metals combine when the nickel is finely divided. Nickel has been used as a constituent of low-grade amalgams, but nickel and mercury

as an amalgam has no practical application.

## Dental for Uses Mercury-

- 1. Added to alloys to form amalgams for filling purposes.
  - 2. Added to fusible alloys to lower the melting-points.
- 3. As the compound vermilion as a colouring agent for rubbers.
- 4. Corrosive Sublimate.—This compound occurs native, and may also be prepared by decomposing mercuric sulphide. This is done by heating it with small quantities of salt, the temperature being gradually increased, when the mercuric chloride sublimes, and condenses on the sides and cool parts of the heating apparatus. A trace of magnesium dioxide is generally added to prevent the forming of mercurous chloride. It may also be prepared by heating mercury in an excess of chlorine gas, or by dissolving mercuric oxide in hydrochloric acid. As mercuric chloride (HgCl<sub>2</sub>), it is used as a germicide, in solutions of I in 2,000 and I in 3,000, in general cavity toilet, washing out roots, and for sterilizing purposes. Care must be exercised in its use, however, as the compound attacks silver and nickel-plating, and gradually steel itself. Platinum nerve canal fillers, nozzles of syringes, etc., are usually employed in applying it about the mouth. The compound is extremely poisonous. Mercurous chloride (HgCl<sub>2</sub>), also known as "calomel," mercurous and mercuric iodide, are best studied under Materia Medica.

Vermilion.— This compound is a crystalline variety of cinnabar, the native sulphide of mercury, and is well known by its characteristic bright colour, the colour generally being brightest when the compound is pure. There are two main processes for manufacturing vermilion.

Chinese Method.— This consists in heating 4 parts of mercury with I part of sulphur in an earthenware vessel, which is covered with an iron plate luted on to exclude the air, and the lid kept damp during the process. The heat is kept up for twenty-four hours, the earthenware vessel broken up, the sublimate of the purest colour selected as the highest grade, and on being washed is ready for use.\*

Dutch Method.— This consists in heating 7 parts of mercury with I part of sulphur, keeping the compound at fusing-point for several hours, and then pouring it on iron hot plates. After being kept fused for several hours, it is allowed to cool. On being broken up and

washed, the vermilion is ready for use.

Various wet methods may be employed.

I. Precipitate mercury from a salt using

r. Precipitate mercury from a salt, using sulphuretted hydrogen, and heat the black sulphide so obtained until it is sublimed. This, on being washed with an alkaline solution of potassium sulphide, yields vermilion of a good colour.

2. Triturate 100 parts mercury with 38 parts sulphur, and digest in a solution containing 25 parts caustic potash and 150 parts water. The mixture is kept as near 45° C. as possible for several hours, water being added to replace that lost by evaporation, when vermilion of a good colour is obtained.†

Properties of Vermilion.— Vermilion when pure contains 86 per cent. of mercury, is very finely divided, and of a bright scarlet colour. The Chinese variety is

<sup>\*</sup> Greenwood.

<sup>†</sup> Turner's "Prosthetic Dentistry."

considered the best for colour and purity. The compound is soluble in aqua regia and sodium sulphide, but insoluble in dilute nitric, concentrated sulphuric, or hydrochloric acid, cyanide of potassium, sulphide of ammonia, or alcohol. It is used largely as a pigment, and for dental purposes for colouring vulcanizing rubbers. It has been frequently blamed for inducing sensitive conditions of the palate when present in base-plate rubbers, especially in those of low grades. Many of such rubbers, when seen under the magnifying-glass, disclose great porosity of the surface, which, on absorbing dirt, may induce irritation. In several rubbers where vermilion is said not to be used as a colouring agent, however, there is generally less complaint on this score. Vermilion in commerce is frequently adulterated with free mercury, red lead, arsenious sulphide, etc., all of which are capable of causing irritation even if present in small traces.

#### CHAPTER V

#### ZINC

Symbol, Zn. Specific gravity, 7:15.

Atomic weight, 65.37. Melting-point, 418° C.

#### Occurrence.

Name.	Composition.	Percentage of Zinc in Pure Mineral.	
Zinc sulphide, or blende	Zinc and sulphur	67	
Zinc oxide, zincite, or red zinc Zinc carbonate, or calamine	Zinc and oxygen	80	
	Zinc, oxygen, and $CO_2$	52	

Also electric calamine, so called because its crystals become polar when heated; Willemite, an anhydrous silicate; Franklinite and Gahnite.

The sulphide, known as "zinc-blende," from the German word blenden, to dazzle, is also known as "black jack," and is the chief source of the metal. It is seldom pure, being generally associated with the sulphides of iron, copper, lead, manganese, and less frequently with silver and cadmium. The ore usually contains from 40 to 60 per cent. zinc. The carbonate is the next in importance, and is the most abundant ore of zinc. It also contains iron, manganese, etc. The other ores, with the exception of the oxide, are less abundant, contain less zinc, and are seldom employed for the extraction of the metals.

Preparation of Zinc.—There are two classes of processes—the dry and wet. Zinc belongs to that class known as "volatile metals," passing into the gaseous state if heated beyond its fusing-point, from which state it is recovered by a process of condensation. The ores to be treated should be rich in zinc, and as uniform in composition as possible, care at this stage simplifying the after-treatment very considerably. Before heating, the ores are carefully picked and washed clean of useless matter, and are subjected to a preliminary calcining at a low temperature. This, in order to drive off as much of the impure matter as possible, converts sulphides into oxides, and breaks up the ore held in its matrix of quartz, etc. The calcining also facilitates the distilling of the metal, and volatile impurities, such as arsenides, etc., which would exert a powerful effect on the properties of the finished metal, are driven off. The calcined ore is mixed with carbon, placed in close fire-clay vessels or in crucibles supplied or connected with some type of condenser to effect the cooling of the zinc vapour. is then heated to 926.5° C.,\* 930° C.,† 940° C.,‡ the boiling-point of zinc, and the temperature gradually increased to 1,300° C. to insure the complete removal of the zinc. The various processes may be classed as—

I. Distillation in horizontal retorts, as in the Belgian method.

2. Distillation in muffles, as in the Silesian method.

3. Distillation in the Belgo-Silesian furnaces.

The English and Carinthian processes are no longer used.§

Belgian Method.—The calcined ore is placed in fireclay cylinders arranged in tiers, all sloping downwards, with as many as eighty cylinders in a tier. The zinc, as it escapes, is led through iron piping to the condenser, where it is collected.

<sup>\*</sup> Greenwood. † Newth. ‡ Essig. § Schnabel and Louis, vol. ii., p. 131.

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The Silesian Method.—The calcined ores are placed in muffles instead of cylinders, as in the Belgian method, it being held that the muffle can withstand a higher temperature than the cylinder without change of shape or fracture, and consequently admits of a more perfect extraction of the zinc. The condensers are generally long iron tubes, into which the vapour passes.

The Belgo-Silesian Method.—This process differs from the processes already detailed only in the arrangement of the muffles and the type of condensing tubes, which have a cup or depression in the base through which the zinc may be tapped. In all these processes some type of reverberatory furnace fired by solid coal or gas is employed for heating the vessels containing the zinc

ores.

The Wet and Electro-Metallurgical Methods.—As zinc cannot be separated from its solutions by any metal not oxidized at ordinary temperatures, the wet methods only admit of the production of compounds of zinc, from which the metal may be extracted by heat. The wet methods are employed only in conjunction with the dry methods. These combined methods have been tried on poor ores, but have been discarded. The electrolytic extraction of zinc is from a solution from which the zinc is separated by means of an electric current. The process is chiefly made use of in the removal of zinc from an alloy, when the alloy may be used as the anodes.

Refining of Zine.—The metal as produced by the dry methods is generally contaminated with traces of such metals as lead, frequently in excess of 5 per cent., and iron about 0·1 to 0·2 per cent. For commercial purposes the lead is removed, as its effect would be to reduce the extensibility of the metal. The zinc is brought to the melting-point very slowly, and after being kept molten for some time it is allowed to cool slowly. The impurities, such as iron, rise to the surface,

and are ladled off, or the zinc is ladled off, leaving the

lead present.

For dental purposes, such as for cement fillings, and as a constituent of amalgams and solders, the pure metal is produced by bringing the zinc to solution, precipitating it with a suitable reagent, and melting the zinc under carbon.

**Properties of Zine.**—The metal has a bluish-white colour, and possesses less metallic lustre than most other metals. Freshly cast zinc, if broken, shows a fracture of a tabular structure, which quickly tarnishes in contact with air. Apart from loss of brilliancy, the air, if dry, has no action upon it, but moist air causes a film of oxide to form, which protects the metal from further oxidation. When heated to redness, it quickly oxidizes, and burns with a bluish flame, giving off a white flocculent powder, the oxide somewhat resembling wool, and at one time known as "philosopher's wool." Carbonic acid acts upon the metal, forming a coating of the carbonate. Hot water tends to oxidize zinc, but cold water, unless it contains CO<sub>2</sub> in solution, has no action.

Pure zinc is not readily affected by the ordinary strong pure sulphuric or hydrochloric acids, but small traces of impurities determine the solution of the metal, hydrogen being evolved. Ordinary commercial zinc, or spelter, as it is called in ingot, is readily attacked by these acids, and can decompose boiling water, giving off hydrogen. Zinc dissolved in hydrochloric acid constitutes the "spirits of salt" used as a flux in soft soldering.

At ordinary temperatures zinc is brittle, but heated to 100° to 150° C. it becomes malleable, and may be readily rolled and hammered. If raised to 205° C. it again becomes brittle, and may be readily reduced to powder. Zinc possesses the property of being readily deposited from solutions, and also that of depositing other metals from solution, such as gold in the cyanide

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processes, silver, and copper. It also lowers the meltingpoint of the metals to which it may be alloyed. The chief use of the metal industrially is as a constituent of alloys, and for galvanizing iron.

**Dental Uses for Zinc.**—I. As a die metal, either alone or alloyed with tin, etc.

2. As a constituent of gold solders to increase fluidity.

3. In dental amalgams chiefly as a substitute for platinum.

4. In the oxyphosphate, oxysulphate, and oxychloride of zinc cement fillings, and in several of its salts, as learned under Materia Medica.

5. In nickel silver, brass, silver solders, etc.

Zinc as a Die Metal.—The metal has long been a favourite for casting dies for swaging plates. Its cheapness, hardness, and the ease with which it can be melted in the ordinary laboratory furnace or Fletcher melting apparatus; its strength, fluidity, and the fact that it may be remelted many times, if ordinary care is exercised, without depreciation of its properties, have brought it into favour. Stress has been put upon the marked contraction of the metal as it cools, but it should be noted that this contraction is largely confined to the base of the zinc model, and also may be greatly reduced if the metal is not overheated, is kept clean, and poured at the proper temperature. The ladle and melting-pot are of iron, and should be kept carefully coated with Paris whiting, chalk, etc., to prevent oxidation of the metal through contact with the iron. Brassmoulders generally test the heat of the alloy by using a billet of wood. If the wood sizzles violently on being plunged into the metal, this is a sign of too great heat; when the wood causes no commotion, the pouring heat has been reached. Zinc may be tested by the same means with good results. Over-hammering is a common cause of change of shape of the die, and most of the striking up of the base-plates should be done before the die and counter-die are brought together. All

traces of scum or oxidized zinc should be carefully scraped clear of the metal before pouring, and care should be taken to keep the metals zinc and lead separate when melting either.

Cleaning Zinc.—When zinc has become contaminated with lead, the metals may be partially separated by bringing the zinc to melting-point, and allowing the metals to cool slowly until set. The lead sinks, and may be chiselled from the zinc. Ordinary dirt may frequently be removed by throwing chips of old wax on to the molten zinc and setting fire to it. The surface should then be well skimmed before pouring the metal.

Ammonium chloride used in the same manner yields good results. When the age of zinc affects its fluidity, hardness, and strength, the addition of I part aluminium to every 9 parts zinc, mentioned by Richardson, also improves the metal. The aluminium is melted, and added to the zinc and well stirred, and the surface ladled clear of débris. The aluminium reduces oxidation, and, when added in small quantities, does not reduce the strength of the zinc.

# Alloys of Zinc.

Zinc .and Lead.—These metals when alloyed constantly tend to liquate. Lead softens zinc, and in small traces is added to commercial zinc to increase ductility.

Zinc and Tin.—These alloy readily, and in various proportions, showing little tendency to separate. Tin is added to spelter zinc for casting purposes, to overcome the brittleness of zinc when hammered; to check contraction; to increase the fluidity of the metal when molten; and to give the casting a smoother surface. Fletcher advocates tin to be added I part to 2 parts zinc; Richardson, I part of tin to 4 parts zinc; while by others equal parts have been advocated.

The 25 per cent. tin gives excellent results, provided

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overheating is avoided. Zinc and tin in equal parts yield an alloy almost equal to brass in density; but as the proportion of tin is increased, deterioration also increases after several meltings.

Zinc and Gold.—These metals are never alloyed without the addition of such metals as copper and silver. Added to gold of various carats, zinc increases the fluidity; hence it is added to many gold solders.

(See Gold and Zinc.)

Zinc and Silver.—Zinc is only added to silver, generally along with copper, to reduce the standard and the fusing-point of silver; it is present, too, in all silver solders. The chief use of the metal, apart from what has been given, is a constituent of cement fillings and dental amalgams.

**Cement Fillings.**—These fillings may be roughly divided into three groups—the oxychloride, the oxyphosphate, and the oxysulphate of zinc. They are pre-

pared from the pure zinc oxide as a base.

The Powder.—The oxide is prepared by the combustion of pure zinc by heating it, exposed to the air to 1,900° F., producing the white flocculent powder already mentioned. It may also be prepared by heating the carbonate of zinc (ZnCO<sub>2</sub>) to redness. If overheated, the resulting powder is yellow in colour instead of white, and is harsh and gritty. The flocculent powder is treated with nitric acid, and calcined at a white heat in fireclay crucibles having the covers luted in place to exclude the air. The calcining is continued for several hours, when it will be found that the powder has contracted considerably, is light yellow in colour, and slightly vitreous. It is then ground to a fine powder, sieved through fine cloth to insure fineness of grit, and bottled. Arsenic, lead, and chalk, are the most common adulterations found in commercial zinc oxide. Pure zinc oxide is soluble in dilute sulphuric acid, any lead and arsenic present being left as a deposit. To bring the powder to the various shades required for dental cements, pure titanium, native oxide of titanium, powdered rutile, ammonium and calcium phosphate, cadmium oxide, etc., are added. The oxides of aluminium, magnesium, tin, and silica, ground glass, borax, etc., are added to improve the wearing qualities.

Oxychloride of Zinc Cement.—The powder is pure zinc oxide, mixed with some of the colouring and vitrifying agents. The liquid is a solution of zinc chloride, and is prepared by deliquescing with distilled water, the proportions being 2 of chloride to I of water. This is allowed a few days to settle, when the clear liquid is decanted.

Feichtinger's\* formula is 3 parts zinc oxide, I part glass powder, 50 parts zinc chloride (specific gravity = 1.5), to which is further added 1 part borax dissolved in the least possible quantity of water. This cement filling, like the others of the group, should be well spatulated with a nickel, ivory, tantalum, or heavily plated steel spatula, as the plain steel tends to cause darkening of the fillings a few weeks after insertion. The oxychloride acts as an irritant to pulp tissue, and, being prepared white as a rule, its use is chiefly confined to lining pulpless and discoloured teeth. On account of its antiseptic properties, it is used as a root canal filling. As the cement is rapidly attacked by the oral secretions, it is never brought to the cavity surface, but covered with gold, porcelain, amalgam, or oxyphosphate of zinc filling.

Oxyphosphate of Zinc.—The powder is the same as for the oxychloride. The liquid is prepared by dissolving pure glacial phosphoric (metaphosphoric) acid in distilled water, and evaporating the solution to a syrupy consistency. This cement is less irritating to pulp tissue than the oxychloride, and is the cement mostly used. It is less soluble in saliva than the oxychloride, resists attrition better, is extremely adhesive, and has many uses.

<sup>\*</sup> Griffith's "Dental Metallurgy," p. 136.

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Oxysulphate of Zinc.—The powder is 3 parts zinc oxide to I part calcined zinc sulphate; the liquid containing gum arabic dissolved in water, with a trace of calcium sulphate. The use of this cement is generally limited to protecting nearly exposed pulps, and lining sensitive teeth to receive metallic fillings. It is also used to relieve sensitiveness during preparation of a cavity, reducing the painful symptoms if left in the cavity a few weeks. It is never inserted as a finished filling, being less permanent than the oxyphosphates. All cement fillings are benefited by a protective coating of varnish or white cement wax before complete hardening has occurred, which generally occupies two hours at the minimum.

Oxyphosphate of Copper.—The powder is pure oxide of copper plus some siliceous ingredients to increase the wear resistance. The liquid is similar to the oxyphosphate. The cement can be obtained either black or in the same range of shades as the oxyphosphate of zinc cements, the black cement being kept away from the front of the mouth. It offers greater resistance to the saliva, and wears better, than the oxyphosphate of zinc, and is of service in filling cavities in deciduous teeth, as a temporary filling in permanent molars, and in those troublesome cavities occurring on the buccal surface of wisdom and molar teeth. The cement sets rapidly, is hydraulic, and does not affect the colour of the tooth by impregnation. The spatula for these cements should be of agate or ivory, and the instruments agate, ivory, or tantalum.

Silicate Cements.—These fillings in their most recent forms present properties which render them valuable in many instances. As a class they are translucent when moistened by saliva and polished; they offer fair resistance to attrition and normal saliva, and the wide range of colours permits of accurate colour matching to the rest of the tooth. It is urged against these fillings that they are less adhesive than the oxyphosphates,

and that they contract. These failings, however, can be overcome to a large extent by making the cavity of a retentive shape, and by careful mixing, as in the case of oxyphosphate. They are best mixed on an agate slab kept solely for this filling, the spatula preferably ivory, agate, or good bone. The instruments used in inserting and shaping the filling should be of bone, ivory, agate, or tortoiseshell; on no account should steel instruments be used for shaping, or steel burs in finishing, as they cause the filling to darken very markedly. The various varieties differ in composition, but they may be held to contain the following:

Powder.—A combination of basic beryllum nitrate, Be(NO<sub>3</sub>)<sub>2</sub>2BeO, and sodium silicate;\* or a compound of silicates of lime and alumina with aluminates, modified by the addition of other basic silicates which the manufacturers may determine advantageous in the production

of desired effects. †

Liquid.—A solution of 52 per cent. orthophosphoric acid and an almost saturated solution of aluminium phosphate, with a trace of zinc or strontium phosphate dissolved in it.

A filling material consisting of a mixture of zinc oxyphosphate, white copper, and the powder of a silicate cement, has been placed before the profession. ‡ It is claimed for this cement that advantage is taken of the adhesiveness of the zinc fillings, the therapeutic and antiseptic properties of the copper, and the insolubility and wear resistance of the silicates. The cement is opaque when hard, is very slow setting, and will require a lapse of time to test its sphere of usefulness.

<sup>\*</sup> Dental Cosmos, April, 1909, p. 442.

<sup>†</sup> *Ibid.*, p. 440. ‡ February, 1915.

#### CHAPTER VI

#### TIN

Symbol, Sn. Specific gravity, 7.30.

Atomic weight, 118.80. Melting-point, 232° C.

**Occurrence.**—Cassiterite, or tinstone (SnO<sub>2</sub>), the most important ore and source of the metal, is found in immense deposits, although in few localities. It is at times found in almost pure nodules of the oxide known as *stream tin ore*. It is usually associated with ores of arsenic, copper pyrites, specular iron ore, wolfram (tungstate of iron and manganese), and other minerals. It also occurs as tin pyrites (SnS), to a lesser extent.

**Preparation of Tin.**—Commercial tin is prepared exclusively from the oxide or tinstone, the process consisting of—

- Crushing the ore and washing it free of earthy matter.
- 2. Calcining in a reverberatory furnace to drive off sulphur as sulphur dioxide, and arsenic as arsenious oxide, which latter is collected by condensation.
- 3. Washing the calcined ore in wooden tanks, when copper sulphate dissolves out, and is deposited by iron plates as "cement copper." Oxide of iron and other light matters are removed as a scum.
- 4. Smelting Process. The smelting of the tin ore is generally carried out in a reverberatory furnace. The furnace charge consists of tin ore mixed with one-fifth its weight of powdered anthracite, a little lime or fluor-spar being added as a flux to carry off any trace of silica

present. The mixture is moistened to cause it to cake together, and the heat gradually raised for five hours. The slag as it forms is drawn off through tap-holes, carrying with it the silicates of iron, etc., and the furnace charge constantly stirred with billets of green wood. The tin is then run into iron receptacles called "kettles." Tin so produced contains traces of several metals contained in the ore, and has to undergo a process of refining.

Blast-Furnace Process.—In Saxony the blast-furnace process is employed for the preparation of tin, the charge of ore, fuel, and flux, being similar to that in the process described above. The furnaces used are small, and the temperature is kept as low as possible, in order to prevent the reduction of other metals. The tin produced has to be liquated and refined. The loss of tin due to oxidation is rather higher than in the reverberatory furnace process.

When wolfram is present in an ore of tin, it is generally removed by special treatment. Soda ash and coal dust are added to the ore, and the mixture heated in a reverberatory furnace. Tungstate of soda is formed, which is removed by washing, and collected by evaporating the solution. The oxides of manganese and iron still in the ores are readily removed by further washing.

Refining of Tin.—The process of separating the tin from the alloyed metals consists of liquation and poling. Liquation of Tin.—The ingots produced by the previous process are heated on the bed of a reverberatory furnace until the melting-point of the tin is reached, when the metal melts and flows away, and is collected in pots, or, as they are called, "kettles," which are heated by a separate fire. Most of the impurities are left on the hearth of the furnace.

Poling of Tin.—The tin is kept at melting-point in kettles, and stirred with poles of green wood; or logs of wet wood are held under the surface of the metal. The steam evolved by the wood sets up a violent action, causing the impurities still present to be thrown out of

combination with the tin; they collect as a scum on the surface, and are then skimmed off. At times "tossing" of the tin is resorted to instead of poling—that is, the tin is raised in ladlefuls and poured back into the kettle. The tin is run into moulds, and allowed to set slowly. The purest tin, known as grain tin, remains on the surface, and may be collected; the central layer is ordinary tin, and the bottom layer is generally put through the refining process again.

Properties of Tin.—Tin is a white metal with a slight tinge of yellow, and when heated emits a peculiar odour. It is among the least tenacious of the metals, but is very malleable, and can be rolled, when pure, into very thin foil with ease. Tin in ingot or bar form shows a crystalline structure on fracture, and if a rod of tin be bent it emits a peculiar sound, referred to as the "cry of tin," due to the crystals of the metal grinding together. Rolling or hammering, while destroying its crystalline structure, does not appreciably increase the specific gravity. The name "grain tin," already mentioned, refers to the peculiar structure of the metal, which is produced by striking the metal with a hammer when on the point of setting, or by dropping a heated ingot from a height and breaking it, the crystalline structure being thus broken up.

Tin is an important constituent of many alloys, such as bronzes, etc. (See Alloys.) It is soluble in alkaline solutions—an important property from a dental standpoint. Strong nitric acid does not dissolve tin, but oxidizes it; dilute nitric acid dissolves tin, nitrous fumes being given off and metastannic acid formed. The metal is also soluble in strong hydrochloric and sul-

phuric acids.

Tin may be deposited from its solutions in the form

of elongated needles by electricity.

Tinning of Iron.—Tin does not oxidize at ordinary temperatures or in moist air—hence its value as a protective coating to articles made of iron. This coating

is referred to as "tinning," and is applied by cleaning the iron surface thoroughly with sulphuric acid and sand, drying thoroughly by dipping the article into molten tallow, then plunging it into melted tin. Several coatings are necessary to insure evenness of the surface.

Putty Powder.—An impure form of tin dioxide known as "putty powder," is produced by heating the metal beyond its melting-point. This powder, yellowish in colour, is largely used for polishing glass and for restoring the polish to artificial teeth, porcelain inlays, fillings, etc.

**Dental Uses for Tin.**—In the laboratory, tin, either pure or alloyed with lead, is used in foil form for taking shapes for metal plates and making polishing plates; in several thicknesses of foil, or in sheet, for try-in plates; pure or alloyed with silver or gold for lower dentures, etc., or alloyed with a trace of lead for suction chambers; and as a constituent of soft solders for special

trays, etc. 185

As a Filling Material.—As a filling material, tin is used pure in foil or cylinders, in much the same manner as gold. It is less cohesive than gold, less malleable, and darkens when exposed to the saliva. The darkening, however, is not transmitted to the tooth structure, as with palladium amalgams. It possesses fair edge strength when not exposed to the full strain of mastication in a compound cavity; does not contract; is low in conductivity, and affords good protection to the tooth against caries. Cavities exposed to the full strain of mastication are frequently based with tin, and surfaced with gold, to afford greater protection. A combination of tin and gold has been introduced, consisting of tin-foil coated with a thin layer of pure gold, in the form of tubes, which may be cut into suitable sizes of cylinders, or worked into the cavity, using the full length of each piece, in much the same manner as non-cohesive foil is worked in rope form. The filling is light in colour, and in conductivity is less than gold. It is restricted TIN 39

generally to simple cavities, and is surfaced with pure gold. Tin has an important position as a constituent

of dental amalgams. (See Amalgams.)

Casting Tin and Tin Alloys for Lower Dentures.—Tin is used either pure or alloyed (see Alloys) for casting lower dentures where the conditions demand increased weight, the process being referred to as the "cheoplastic process." It may either be carried out using such a form of flask as Gartrell's for the purpose, or a modified flask, as for vulcanite cases, or a ring, as employed for the casting machines, either by air-pressure or vacuum. The denture is waxed up carefully, having a sprue attached to either extremity, and smoothed over with chloroform, and invested in the flask or casting-ring in equal parts of casting investment and plaster, the same care being exercised as when investing for gold casting. On setting, the wax is either boiled or roasted out, and the investment raised to a sharp heat to expel moisture, wax, etc. The investing ring or flask should never be at a red heat when the casting is being run, a "juggling" heat being quite sufficient. The alloy selected is melted in a separate crucible, and either poured into one of the sprue-gates until the metal is seen to appear at the other sprue-gate, or poured rapidly from the crucible and the air-pressure applied, or the key of the vacuum pump released. An interval of ten minutes at least should elapse before opening the casting.

Alloys for this purpose should possess certain prop-

erties:

I. They should not discolour in the mouth.

2. They should be non-irritating to the mucous membrane and non-poisonous.

3. The fusing-point should not be very high, so as to

reduce chance of fracture of the teeth in firing.

4. They should lend themselves to being rapidly repaired.

The alloys for this purpose are generally composed of tin and silver, with copper or gold added as modifying metals to overcome expansion or contraction and to improve the colour. The same care is necessary in melting them all, avoid overheating, use clean fire-clay crucibles, or clean iron spoons, for such alloys as Gartrell's, acolite, Watt's, or Weston's New Metal. Most of these alloys are proprietary, but the formulæ for the following alloys are known:

Bean's alloy for casting lower dentures: 95 parts tin,

5 parts silver.

Reese's alloy for casting lower dentures: 20 parts tin, 1 part gold, 2 parts silver.

Kingsbury's alloy for casting lower dentures: 16 parts

tin, I part antimony.

Acolite, Watt's and Weston's new metal, can be employed for inlays in posterior teeth, and for restoring surface of teeth extending below the normal gum margin previous to crowning.

Tin alloys readily with gold, but tin beyond 10 per

cent. renders the gold brittle.

If alloyed with platinum or palladium, the alloy is hard and brittle. Silver and tin alloy readily, and an alloy of these metals containing 20 parts tin and 80 parts silver is tough, and is not brittle. Tin exerts a wonderful effect when alloyed with all these metals, lowering their fusing-points. The metal also has a wonderful affinity for gold and platinum, combining with explosive violence with platinum if the two are rolled together and melted under the blowpipe (Turner).

## Alloys of Tin.

Babbit metal: Antimony 22·3, copper II·I, tin 66. Turner's formula is: Tin 24, antimony 8, copper 4.

Haskell's metal: tin 8, antimony 2, copper 1.

Fletcher's metal: Tin 70.6, antimony 17.64, copper 11.76.

Britannia metal (1) contains 42 parts tin, 3 parts

antimony, I part copper, and I part bass.

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Britannia metal (2) contains 90.7 parts tin, 7.8 parts antimony, 1.5 parts copper.

Pewter metal contains 79 parts tin, 15 parts antimony,

6 parts lead.

Bronze contains copper, tin, and zinc, in varying pro-

portions. (See Copper.)

Meter metal, an alloy of tin and lead plus a trace of antimony, is used instead of tin-foil for swaging trial and polishing plates.

#### CHAPTER VII

#### **CADMIUM**

Symbol, Cd. Specific gravity, 8.60.

Atomic weight, 112.4. Melting-point, 322° C.

Occurrence.—In the process of zinc extraction it was observed that a brown-coloured volatile vapour was in most cases distilled over with the first portion of the zinc. This, on examination, was found to be the metal cadmium. It is chiefly obtained as a by-product in zinc extraction, especially if zinc-blende and calamine are being reduced, when the yield is about 0·3 per cent. cadmium.

It is found as a native sulphide (CdS), containing 77.6 per cent. cadmium, and known as "greenockite" in Renfrewshire, Scotland.

Preparation.—Cadmium at the present time is only

prepared by dry methods on commercial scales.

Extraction of Cadmium by Dry Method.—Advantage is taken of the fact that cadmium oxide is reduced to the metallic state at a lower temperature than zinc and that cadmium also volatilizes at a lower temperature than does metallic zinc. The dust which passes over during the first two hours during the extraction of zinc is what is used, and is found to contain from 6 to 8 per cent. cadmium. This is mixed with coal, and heated in retorts to redness, the cadmium passing into long sheet-iron cones where it collects. As this contains traces of zinc and zinc oxide, it is again mixed with charcoal, and distilled in small clay or cast-iron retorts

fitted with long sheet-iron adapters, where the cadmium is removed in the metallic state. Pure cadmium may be obtained by dissolving zinc and cadmium in dilute sulphuric acid, and passing sulphuretted hydrogen through the solution, thus precipitating the cadmium as the pure sulphide. The sulphide is dissolved in strong hydrochloric acid, and carbonate of ammonia added. Cadmium carbonate is formed, which, distilled with charcoal, yields pure cadmium.

Properties of Cadmium.—Cadmium is a white metal with a bluish tinge, dense in structure, and crystallizes in the forms of the cubical system. The metal is soft and ductile, and can be rolled into very thin foil or drawn into fine wire. It is generally met with as rods about 3 inches long, which "cry" like tin when bent. Cadmium is soluble in hydrochloric, sulphuric, and nitric acids, the latter dissolving it rapidly. It is also acted upon by alkaline solutions, and sulphuretted hydrogen acts on the metal, forming cadmium sulphide.

Cadmium added to amalgams hastens the setting, also rendering them more plastic. It was formerly used in dental amalgams, but the blackness of the resulting filling, the formation of cadmium sulphide on the surface, and the solvent action of alkaline solutions on the

metal, led to its disuse.

Its chief use at present is as a constituent of the fusible metals. Added to alloys, cadmium possesses the property of lowering the melting-points to a remarkable degree. Thus, an alloy containing 8 parts lead, 15 parts bismuth, 4 parts tin, and 3 parts cadmium, melts at 60° C., and is quite fluid at 65° C.\*

Cadmium has lately been used for electro-deposition as an alloy with silver in place of ordinary silver-plating.

For other alloys, see Fusible Metals.

<sup>\*</sup> Lipowitz, Dingler, vol. clviii., p. 376.

### **BISMUTH**

Symbol, Bi. Atomic weight, 208 o. Specific gravity, 9-80. Melting-point, 268 °C.

**Occurrence.**—This metal occurs native to a considerable extent, native bismuth being, in fact, the chief source of bismuth.

Bismuth ochre  $(\mathrm{Bi}_2\mathrm{O}_3)$  contains 87 per cent. bismuth, with traces of arsenic, copper, and iron. Bismuth glance  $(\mathrm{Bi}_2\mathrm{S}_3)$ , the sulphide, contains 81 25 per cent. bismuth.

Bismuth copper glance  $(3Cu_2S + Bi_2S_3)$ .

**Preparation.**—Bismuth is extracted by dry and wet process, the electrolytic process not having yet been

adopted to any great extent.

Dry Methods—Extraction of Bismuth by Fusion Processes.—The bismuth is either separated by liquation Of these the fusion process is more complete, or fusion. admitting of the addition of reducing or desulphurizing agents, which, while removing the metallic bismuth, also extract the bismuth and sulphur and the bismuth compounds. Crucible furnaces are generally employed in the fusion process; carbon is added to reduce the oxides, iron to absorb the sulphur, and an alkaline flux to combine with any gangue present. The bismuth is melted and poured into iron moulds. The metal collects at the bottom, covered by a speiss containing arsenic, nickel, traces of cobalt, and the slag, from which the bismuth is run off, the speiss and the slag setting more rapidly.

Extraction of Bismuth by Wet Method from the Ore.\*— The ore is first roasted to drive off the arsenic and sulphur, and transferred, while hot, from the furnace to wooden troughs, where it is dissolved in dilute hydrochloric acid. The oxychloride of bismuth so formed is

<sup>\*</sup> The Mineral Industry, 1896, p. 55.

precipitated by the addition of water. If any lead or iron is present, the precipitate is again dissolved in dilute hydrochloric acid, and precipitated with water. The precipitate is washed, dried, and mixed with charcoal, slag, and some lime. The bismuth may also be precipitated from the hydrochloric acid solution by metallic iron. It is then melted in graphite crucibles, producing metallic bismuth.

**Properties of Bismuth.**—Bismuth is grey-white in colour, with a decidedly reddish tinge and a bright metallic lustre, which is not affected by exposure to the atmosphere. The metal is rapidly oxidized by heat, and, at a temperature above its melting-point, burns with a bluish flame, giving off yellow fumes of the "flowers of bismuth," a property also possessed by antimony. Bismuth is extremely brittle, and can be readily reduced to powder. Like antimony, it crystallizes in rhombohedrons, is strongly diamagnetic, possesses the peculiar property of expanding when cooling, and has a higher specific gravity when liquid than when solid. It is vigorously attacked by nitric acid, bismuth nitrate being formed, which, diluted with water, forms the insoluble basic nitrate of bismuth. The impurities present in the metal are traces of arsenic and sulphur, also copper, cobalt, gold, silver, and nickel, the silver having been found present in as high a proportion as 60 ounces to the ton.\* The brittle quality of the metal prevents its separate use. Advantage is taken of this property of expanding on cooling, its low fusing-point, and its consequent lowering of the fusing-points of the alloys to which it is added. It is added, for example, to type metal and stereotype metal, because of its property of expanding on cooling, as it gives a much finer casting owing to the absence of any contraction. It is made use of mostly in the group of low fusing-point alloys known as "fusible metals," which are dealt with

<sup>\*</sup> Greenwood

in another chapter. Bismuth added to gold or silver renders the metal brittle and unworkable. Added to lead in the proportion of 3 parts of lead to 2 parts of bismuth, it yields an alloy said to possess ten times the strength of lead. The action of the metal, like antimony, is to harden whatever metal it may be added to. It is never added to dental amalgams, as it increases the quantity of mercury required to form the amalgam, besides imparting to it a sticky quality. Fletcher states that an amalgam of I part bismuth, I5 parts tin, I5 parts silver, fused, filed up, and mixed I part alloy to 4 parts mercury, will adhere to a flat dry surface, and may be used as a metallic cement for joints in apparatus which require to be perfectly air-tight and stand heavy pressure.

Bismuth is contained in some forms of Britannia metal, Queen's metal, and in the solder used for pewter.

### **ANTIMONY**

Symbol, Sb. Atomic weight, 120°00. Specific gravity, 6°71. Melting-point, 632° C.

Occurrence.—Antimony glance (Sb<sub>2</sub>S<sub>3</sub>), the sulphide, is the chief source of the metal. It is also known as "grey antimony ore," "antimonite," and "stibnite." It contains about 71.77 per cent. antimony and 28.23 per cent. sulphur.

Oxide of antimony (Sb<sub>2</sub>O<sub>3</sub>), also known as "white antimony ore" and "antimony bloom," contains 83.4 per cent. antimony and 16.6 per cent. oxygen. It is formed by weathering of the sulphide or of native antimony, and is less abundan than the sulphide.

Red antimony ore  $(2Sb_2S_3 + Sb_2O_3)$ , also known as "antimony blende" or "pyrostibnite," contains 75 per cent. antimony. Antimony ochre, or cervantite  $(Sb_2O_4)$ , native antimony, etc., are even less abundant sources of

the metal. Antimony is also found present in many of the nickel, lead, silver, and copper ores.

**Preparation.**—At present the dry methods alone are employed for extracting antimony from the ore, the wet methods and the electro-metallurgical processes not

having as yet found practical application.

The ore used most frequently is the sulphide, and advantage is taken of the comparatively low fusing-point of antimony to liquate the metal. The ore is seldom reduced further than pieces of walnut size, the finer the ore is ground the less complete being the separation. The liquation is effected either in pots, reverberatory furnaces, or tubes, the temperature being kept as near the liquating-point of the metal as possible. As the antimony melts, it is collected as a form of crude antimony containing an excess of sulphur. It is then mixed with twice its weight of scrap iron or iron filings enclosed in cone-shaped crucibles, and heated to a higher temperature. The sulphur combines with the iron; the antimony fuses, and is tapped off. Or the purified sulphide may be heated to form the oxide, which in turn may be reduced by charcoal.

**Properties.**—Antimony is bluish-white in colour, with a brilliant lustre; is crystalline and brittle, being readily reduced to powder by hammering. It crystallizes in the rhombohedral system, the surface of the metal exhibiting characteristic fernlike markings. The metal is slowly volatilized if raised to a white heat and exposed to an atmosphere of hydrogen. It is not sensibly affected by ordinary temperatures, or even in the atmosphere, but at a red heat burns with a bluish-white flame, the oxide  $(\mathrm{Sb}_2\mathrm{O}_3)$  being formed. Weak sulphuric acid has no action on the metal, but if heated with strong sulphuric acid the sulphate is formed and sulphurous anhydride given off. Hydrochloric acid has no action on the metal in the mass, but when added to the powdered metal hydrogen is evolved. Nitric acid

causes the metal to oxidize rapidly, but does not dissolve it. Antimony generally has a hardening effect if added to or present in another metal (see Gold), and causes it to expand slightly on cooling. Its chief use in dental metallurgy is in an important series of alloys used as dies and counter-dies. The salts of antimony being poisonous, the metal is never added to dental amalgams.

# Alloys containing Antimony.

Pewter.—Antimony 15, lead 6, tin 79 per cent.

Type Metal.—1. Antimony 25 parts, lead 75 parts.

2. Antimony 18 parts, lead 70 parts, tin 10 parts, copper 2 parts.

3. Antimony I part, lead 8 parts, tin I part.

Either of the above alloys, especially that containing tin, makes a useful alloy for dies and counter-dies. It is especially useful for counter-dies, as, being harder than lead, there is less chance of spreading or distortion of the counter-die during the swaging of base-plates, etc. The alloy melts at a lower temperature than zinc, and besides showing a constant tendency to liquate, has to be very carefully heated to prevent driving off the antimony. The alloy containing no tin is more brittle, and, when employed as a die, should be struck as seldom as possible. This alloy discloses no tendency, when freshly made, to contract.

Antimony is also present in Britannia and Queen's

metals, and in many of the fusible metals.

Antimony added to gold 0.05 per cent. renders the gold brittle and unworkable. Added to iron, 0.1 to 0.3 per cent. renders iron both cold and red-short.

**Die Metals** — Babbit Metal. — Antimony 22.3, copper 11.1, tin 66 per cent. Another formula is given in Turner's "Prosthetic Dentistry." Its contents are given as antimony 8, tin 24, copper 4.

Haskell's Metal.—Antimony 2 parts, tin 8 parts,

copper I part.

Fletcher's Metal.—Antimony 17.64, tin 70.60, copper

11.76 per cent.

Babbit Metal.—There are several formulæ for this useful alloy. In preparing the alloy, half the tin is melted, the antimony, then the copper added, and lastly the rest of the tin. The alloy is whitish in colour, almost like German silver, and has a lower melting-point than zinc. Compared with zinc, there is less contraction, and a cast of this alloy withstands more swaging without change of shape. The alloy should be carefully melted at each heating, and never allowed to reach a red heat, as the tin and antimony are oxidized, and the properties of the alloy completely altered. In casting the alloy, it should be well stirred before pouring, to insure the complete mixing of the component metals. Expense is greatly against the use of this alloy, besides which the constant tendency of the metals to separate is troublesome. When used with a counter die of tin or Babbit metal all risk is avoided in contaminating gold by lead. When lead is used as a counter-die, the die of Babbit metal should be well coated with a thick paste of whiting to prevent the lead softening the surface of the die, and the lead heated to fusing-point, and no further. The alloy is made use of industrially for certain classes of bearings, etc.

Spence's Metal is a non-metallic compound containing the sulphides of iron, lead, antimony, and zinc, dissolved in sulphur. The proportions of these metals vary according to the purpose to which the compound is put. Thus, for dental use it is generally the sulphide of iron dissolved in an excess of sulphur. In colour it is black, is very brittle, melts at a low temperature, shows no contraction on setting, and, if carefully treated, remains stable in composition for a long time. It may be used for the finishing die in metal work, and gives the best results when used with some form of swager. It is also useful for casting impressions for fused porcelain inlays where the matrix has to be swaged to the cast. It sets

rapidly, is sufficiently strong in the edges, and flows well. The brittleness of the compound is against its general use, and overheating drives off sulphur, thus reducing

the strength of the compound for die purposes.

Brass.—This alloy was formerly used for dies, but its high melting-point, the constant tendency of the metals to separate, and the deterioration caused by frequent heatings, led to its disuse. Zinc either as spelter zinc or with 10 per cent. aluminium added is mostly employed for dies in metal work. (See Zinc.)

Fusible Metals.—The term "fusible metal" has come to be associated with a group of low fusing-point alloys, used for purposes such as—

1. For dies and counter-dies in ordinary gold-plate

work.

2. For casting directly into impressions, in cases where an absolutely rigid and accurate model is necessary, as in bridge and crown work.

3. For casting dies for metal crown tops, where crowns

are made in two pieces.

4. For dies in ordinary vulcanite work, where the tin try-in plate is swaged to the die.

5. For weighted lowers casting by gravitation.6. For weighted lowers casting under pressure.

7. For effecting temporary repairs in dentures.

8. As safety plugs for vulcanizers.

These alloys generally contain tin, bismuth, lead, and cadmium, and for weighted lowers, tin, silver, and gold.

The list on p. 51 gives the contents of several of these alloys for die and counter-die purposes, etc.

These are all useful alloys, provided care and dis-

crimination is exercised in using them.

They are easily prepared by bringing the metals together and melting in a well-tempered crucible under a layer of charcoal, and well stirring together with a piece of wood. Mercury is at times added to the alloys employed as dies and counter-dies to still further reduce the melting-points.

Besides being useful for the purposes detailed above, they are of great service in tempering delicate-pointed instruments, or where great accuracy in the temper is required. The instrument to be tempered is laid on a block of an alloy whose fusing-point coincides with the temperature best suited for the instrument, and heat is applied. When the alloy melts, the instrument is withdrawn and cooled. (For temperatures for tempering, see Steel.) They are also used as safety-plugs for vulcanizers, steam-boilers, etc., and usually as an additional check on the steam-gauge or governor. Should the temperature rise too high, and the gauge or governor fail to act, the alloy, being in direct communication with the steam-chest, melts when its fusing-point is reached, letting free the steam.

Fusible alloys have a marked tendency to separate on cooling, and give better results if they are melted under charcoal, and well stirred each time they are brought to the fusing-point.

Name.	 Bismuth.	Tin.	Lead.	Cadmium.	Melting- point, ° C.
Lipowitz alloy Wood's alloy Lichtenberg's alloys Rose's alloy Crouse's alloy Newton's alloy Fusible alloy Brophy's alloy Fusible alloy.	 5 15 5 7 8 8 8 12 48 4	2 4 2 7 3 5 3 2 10 26 12	3 8 4 13 8 5 5 	2 3 2 2 	60 65 71 75 79 88 95 95 98 158

#### CHAPTER VIII

### **SILVER**

Symbol, Ag. Atomic weight, 107.88. Specific gravity, 10.53. Melting-point, 962° C.

**Occurrence**—Native Silver.—Silver is occasionally found native in masses weighing several hundredweights. It usually contains gold, copper, mercury, and other metals; is always present in native gold; is found combined with chlorine, bromine, iodine, and sulphur, and of a silver-white colour in laminated or filamentous masses; also in cubes, crystals, or grains.

The following may be regarded as the more important natural compounds of silver:

Name.	Formula.	Percentage of Silver.
Argentite, or silver glance Kerargyrite, or horn silver . Pyrargyrite, or ruby silver ore Proustite, or light red silver ore Stephanite, or brittle silver ores	$egin{array}{l} Ag_2S \\ AgCl \\ 3Ag_2S.Sb_2S_3 \\ 3Ag_2S.As_2S_3 \\ 5Ag_2S.Sb_2S_3 \end{array}$	87 75 60 65•5 68•5

**Preparation of Silver.**—The processes for the reduction of silver from the ore are somewhat numerous and varied, and the process selected depends upon the

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form or combination in which the silver is present. They may, however, be divided into three classes, as follows:

I. Amalgamation with Mercury. — This process is based upon the solubility of silver in mercury, and the readiness with which the mercury can be driven off by heat.

2. The Lead Methods.—These processes depend on the readiness with which silver and lead combine, the lead being separated after the extraction of the silver from

the ore by cupellation.

3. The Wet Methods.—In these processes the silver is extracted from its sulphides by first converting them into sulphates or chlorides, then washing them out with water or a solution of common salt, and depositing the silver from this solution.

I. Amalgamation Methods.—The ores best adapted for treatment by this process are comparatively free from base metals, and known as milling ores. There are three methods—the Mexican method of amalgamation heaps; the European method of amalgamation in casks, known as the "barrel process"; and the amal-

gamation in kettles and pans.

The Mexican Method.—This process depends upon the solubility of silver in mercury, and the power of the mercury to decompose certain compounds of silver by forming a solution from which the silver can afterwards be extracted. The ores are picked free of any portions containing chlorides, bromides, or iodides, or native silver, which, being the richest, are reduced separately. The ores are then picked free of the ore too poor to repay treatment, washed and placed in tanks or pits, and reduced to powder by crushing. The powdered ore is dried and piled in heaps on a concrete floor covered with from 3 to 5 per cent. common salt, and mixed by mules treading upon it. This is continued for the greater part of one day; mercury is added, with I to 2 per cent. of roasted copper pyrites, known as magistral,

and stirred at intervals for several days. The chemical action taking place is complex, but may be represented thus:

$$\begin{array}{l} {\rm CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4.} \\ {\rm 2CuCl_2 + Ag_2S} &= {\rm 2AgCl + Cu_2Cl_2 + S.} \\ {\rm Ag_2S + Cu_2Cl_2} &= {\rm 2AgCl + Cu_2S.} \end{array}$$

The silver chloride dissolves in the sodium chloride, and is reduced by mercury, mercurous chloride being formed, which passes off with the water—

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag$$
.  
 $Hg_2Cl_2 + Cu = CuCl_2 + 2Hg$ .

The mass is transferred to stone vats, and water and mercury added, the water carrying off adhering particles of minerals and mercuric chloride. The excess of mercury is removed by straining the amalgam through canvas bags, and the silver residue is freed from the

mercury by sublimation.

Amalgamation in Barrels—The Freiburg Process.—This process is most suitable for the treatment of rich sulphide ores, or such as contain sulphides of iron, antimony, bismuth, etc. Iron pyrites is added to bring it up to 25 per cent., and 10 per cent. common salt is added. The mixture is roasted in a reverberatory furnace to drive off arsenic, some of the sulphides, etc. The roasted mass is reduced to a powder, placed in barrels partly filled with warm water, and the barrels caused to revolve. The action may be expressed thus:

$$2AgCl + Fe = 2Ag + FeCl_2$$
.

Mercury and a little copper sulphate are added, and as the amalgam settles it is drawn off.

This process is held to entail no greater loss than 9 per cent. of the silver in the ore, compared with 12 to

25 per cent. in the Mexican method.

Amalgamation in Kettles.—Known as the hot method. The ores are reduced in kettles made with copper bases. As in the other processes, the ore is reduced to powder,

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and the silver is converted into the chloride by adding common salt and mercury; water is added, and the mixture heated to the boiling-point. The copper of the kettle induces the deposition of the silver dissolved out by the mercury, and the mercury is expelled by distillation.

2. Lead Methods.—In these processes the silver is concentrated in lead, and separated by cupellation; or the ore is melted with ores of iron, lead, or copper, and the products cupelled. (See Pattison and Parkes Processes under Lead.)

3. Wet Methods.—These processes are based upon the conversion of the insoluble silver compounds into a soluble form, and precipitation of the silver by means of another metal, such as copper; or precipitating it as

the readily decomposed sulphide.

The Ziervogel Method.—In this the ore is roasted to convert the copper and iron into insoluble oxides, while the silver as the soluble sulphate is removed with warm

water, and deposited by means of scrap copper.

Percy-Patera Method.—In this the ore is roasted with common salt, forming silver chloride, which is extracted by adding sodium thiosulphate. To this solution sodium or calcium sulphide is added, precipitating silver sulphide. The silver is obtained by roasting the sulphide in a

reverberatory furnace.

Russel Method.—In the Percy-Patera process any lead sulphate present is deposited with silver as lead sulphide, and to obviate this, sodium carbonate is added to the solution, after the solution of the chloride in sodium thiosulphate. This deposits as insoluble carbonates any lead, zinc, iron, or manganese, present. The liquid containing the silver and copper in solution is then treated as in the Percy-Patera process.

Electro-Metallurgical Processes.—These processes are confined to the extraction of silver from alloys in the wet methods, the silver being recovered from the slimes left after the removal of the other metal or metals. In

some works where lead is produced, the silver is concentrated in lead, and afterwards cupelled. In the Moebius process the dried slimes are melted and cast into anode plates, the cathodes are copper, and the electrolyte is either an acid solution of copper nitrate or copper sulphate. A current of low tension transfers copper from the anode to the cathode; silver, gold, and platinum, come down as a mud. This mud is collected and parted electrolytically.

Refining of Silver.—The silver produced by these processes has generally to undergo refining to bring it to the standard of "fine silver." The means adopted is generally some form of scorification and cupellation processes, as described under Gold. In these the idea is to concentrate the silver in a mass of lead, and keep the alloy melted until the lead has oxidized into litharge, and passed into the bone ash body of the cupel. The silver is then dissolved in nitric acid, common salt added to form the chloride, the chloride washed and placed in a dilute solution of hydrochloric acid, and silver deposited by means of sheets of clean malleable iron. Or the chloride may be placed in a dilute solution of sulphuric acid, and the silver deposited by sheets of clean zinc. The silver thus produced generally ranks as 999 parts pure in 1,000, the trace of impurity being copper or iron.

**Properties of Silver.**—Silver is remarkable for its whiteness, and, although iridium is also white, its colour in comparison is much inferior. Silver possesses a brilliant metallic lustre, and is only exceeded in malleability and ductility by gold, having been reduced to foil  $_{10000}$  inch in thickness. For swaging purposes, and for being drawn into wire, the metal requires more frequent annealing than gold; otherwise it discloses a tendency to become brittle. In hardness it occupies a position midway between gold and copper, the degree of hardness being influenced by the presence of impurities.

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A single grain of pure silver has been drawn into wire 400 feet long,\* and the tenacity of the metal is given as 7·I tons per square inch. The specific gravity of silver may be increased from IO·53 to IO·57 by hammering or rolling. Silver is the best conductor of heat and electricity, but the presence of impurities has a very marked effect upon the conductivity. The metal melts at a white heat (962° C.), is volatilized at a high temperature, and when heated in the oxyhydrogen flame the vapour given off is of a pale blue colour, inclining to

purple.

The blackened appearance of silver articles after exposure to air is not due to oxidation in the ordinary sense, but rather to a coating of the sulphide formed by the action of the sulphuretted hydrogen of the air. This blackening is also specially remarked in amalgam fillings containing a large percentage of silver. occludes oxygen freely, absorbing twenty-two times its volume of oxygen when in the molten state, but yielding the gas as it becomes solid, the surface rising into protuberances or small craters, each giving out oxygen when it bursts. The phenomenon is referred to as the "spitting" or "vegetation" of silver. The addition of small quantities of copper to silver for casting purposes overcomes this spitting, which tends to destroy the surface of the castings. By covering the molten metal with a layer of common salt, 3 or 4 inches in thickness, the metal sets with a clean, bright, and smooth surface, the salt reducing the occlusion of oxygen, and so preventing the spitting. When heated to redness, silver occludes 0.545 its volume of oxygen. Dr. Percy states that silver alloyed with one-third its weight of gold still occludes gases and spits on setting; but as the gold is increased beyond this, the occlusion and spitting are reduced and disappear.

Silver decomposes sulphuretted hydrogen at ordinary temperatures, the metal being covered with a layer of

<sup>\*</sup> Percy's " Metallurgy."

argentic sulphide. Use is made of this property in "oxidizing" silver articles, the articles being boiled in a solution of potassium sulphide until the desired shade of darkening is reached. Silver combines with bromine, chlorine, and iodine, at ordinary temperatures, the bromide, chloride, and iodide, being formed. Nitric acid is the best solvent of the metal, silver nitrate being formed and oxides of nitrogen given off.

Dilute sulphuric acid has practically no action on the metal, but strong sulphuric acid is decomposed when heated with silver, giving off hydrogen and sulphur dioxide, and forming silver sulphate. Advantage is taken of the action of the acids in parting silver from gold, the gold being insoluble in either of the acids.

(See Sulphuric Acid Process—Gold.)

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$$
.

The Dental Uses for Silver are many. In the pure state in wire form it is used for sutures in fractures of the maxillæ, and in cases of malocclusion, etc., the softness of the metal and its cleanness when in contact with raw tissue or mucous membrane being appreciated. Pure silver in the form of cylinders is used for expressing surpluş mercury from fillings by absorption—a little less rapidly than gold cylinders. It is the use of the metal when alloyed that is most important, such as the alloy with silver, gold, platinum, copper, tin, aluminium, zinc, and the groups of alloys used as dental amalgams.

# Alloys of Silver.

In the pure state silver is too soft for commercial purposes. British silver coinage contains 75 parts copper per 1,000 parts pure silver; Continental silver coinage, 100 parts copper per 1,000 parts pure silver. Mexican dollars contain 337.14 grains pure silver to

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40.65 grains pure copper; United States dollars contain 371.25 grains pure silver and 41.25 grains pure copper.\* Coin or "standard" silver is generally pure silver plus

10 per cent. copper.

Silver and Gold.—The metals alloy freely, but do not appear to enter into chemical combination. Gold is frequently added to silver alloys to reduce the tendency to oxidation of the surface by the formation of the sulphide; but as a rule silver is added to gold, and is detailed under Alloys of Gold.

Silver and Platinum.—These metals alloy freely, the resulting alloys being of a white colour, though

duller than silver.

Dental Alloy contains from 3 to 15 grains of platinum per pennyweight of silver. The alloy is used for baseplates, backings, clasps, pivot-posts, strengtheners, etc. In colour it is greyish-white, is less liable to oxidation than silver, is harder, stronger, and possesses greater elasticity. The fusing-point is high, from 1,750° F. to 2,150° F. permitting the use of 16 and 18 carat gold solder. The use of silver solder with this alloy is not to be recommended, as, although the silver solder more closely approaches the colour of the alloy. it oxidizes rapidly, becoming almost black. The proportions of platinum in the alloy are subject to great variations, ranging in some samples from as low as 10 and 12 per cent. to over 25 per cent., as in that supplied for pivot-posts. The alloying of silver and platinum is readily accomplished if the silver is brought to fusing-point and the platinum added as foil or thin ribbons, the silver absorbing the platinum. The metals do not disclose any distinct tendency to liquate, and after being gently stirred the alloy may be run into ingots and allowed to set. The best results are obtained in annealing if the alloy be kept at a bright red heat for a few seconds before cooling. The best pickling solution

<sup>\*</sup> Turner's "Phosthetic Dentistry."

for dental alloy is a dilute solution of sulphuric acid cold or hot, slightly weaker than for gold. The enhanced cost of platinum has led more or less to its disuse, as the cost

is equal to 16 and 17 carat gold.

Von Eckart's Alloy, used in France for the same purposes as dental alloy, contains silver, 3.53; platinum, 2.40; copper, 11.71.\* It is very elastic, white in colour, and takes a high polish and may be soldered with 15 carat

gold solder.

Silver and Copper.—Copper added to fine silver increases the hardness, tenacity, and strength. The hardest alloy of the two metals contains I part copper to 4 parts silver. Copper, unless added in greater proportions than 40 to 50 per cent., does not alter the colour of the silver; and if added above this proportion, the alloy tends to liquate. Levol's homogeneous alloy containing 718-93 parts silver per I,000 parts alloy, does not tend to liquate. The density of silver and copper alloys is less than the mean density of the metals present, owing, it is held, to expansion occurring as they combine.

Silver and Zinc.—These metals exhibit a decided affinity for each other, and alloy readily. Zinc is seldom added alone to silver, but generally as a constituent of brass, as in silver solder.

Silver and Mercury.—These metals also exhibit a decided affinity, mercury, if present in sufficient quantities, dissolving silver, as has been described under the Amalgamation Processes for the extraction of silver. The two metals are seldom, if ever, amalgamated, for dental purposes, the silver being alloyed with tin, gold, platinum, etc. (See Dental Amalgams.)

**Silver Solders.**—These are generally composed of fine silver or standard silver plus brass or copper and brass. "Standard silver" (pure silver plus 10 per cent. copper) alone makes a high-grade solder for the better qualities of nickel silver and brass, or 6 parts standard

<sup>\*</sup> Essig and Koenig, p. 207.

silver plus I part brass does well for the same purpose. The best-known silver solders contain—

No	. ı.*		No.	4.	
	••		Fine silver ,, brass ,, zinc ,, copper		20 parts. 10 ,, 5 ,, 1 part.
No	. 2.*		No	. 5.	
Fine silver ,, copper ,, brass	••	6 parts. 2 ,, 1 part.	Fine silver ,, brass ,, zinc		4 parts. 2 ,, 1 part.
No	0. 3.		No	. 6.	
Fine silver ,, brass		4 parts.	Silver coin Zinc		9 parts. 1 part.

The same rule applies to the soldering with silver solder as applies to a gold solder—namely, that it should be chosen with a lower fusing-point than the article to be soldered. The greater the proportion of brass to silver, the lower the fusing-point of the solder. Borax acts as a good flux for use with these solders.

Electro-Deposition of Silver.—The bath is of double cyanide of silver and potassium, and the process is generally worked cold. The silver cyanide is prepared by depositing silver from a solution of silver, using nitric acid and cyanide of potassium, which precipitate is soluble in excess of potassium cyanide. To facilitate the plating the metal is coated with a thin layer of phosphorus, the phosphorus reducing the silver nitrate more readily. Or the articles to be plated, after being washed in dilute nitric acid, or aqua fortis, are dipped in a solution of nitrate of mercury until they are coated with a thin layer of mercury. The positive pole is connected with a series of silver plates, while the article to be plated is connected with the negative. Iron and zinc articles are benefited by a previous

<sup>\*</sup> Richardson's "Mechanical Dentistry."

plating of copper or a coating of bronze, the silver adher-

ing better, and showing less tendency to chip.

Dry Silvering.—The process known as "dry silvering" consists in applying an amalgam of silver to a clean surface of metal, and heating to expel the mercury. Another process consists in making the surface of the metal thoroughly clean by using aqua fortis and pumice; the surface is roughened with a graver, so that the silverfoil may adhere to it. The metal is then heated until a thin blue film of oxide forms on the surface, when the silver-foil is tightly burnished to place, the heating being repeated before each layer of the foil is applied.

#### CHAPTER IX

#### COPPER

Symbol, Cu. Specific gravity, 8.82.

Atomic weight, 63.2. Melting-point, 1,084° C.

#### Occurrence-

Composition.	Copper in 100 Parts of Pure Ore.*
Copper, oxygen—Cu <sub>2</sub> O	89
Copper, oxygen—CuO	80
Copper, sulphur—Cu <sub>2</sub> S	8o
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	variable
Copper, iron, sulphur— Cu <sub>2</sub> SFe <sub>2</sub> S <sub>3</sub>	35
	Copper, oxygen—Cu <sub>2</sub> O Copper, oxygen—CuO Copper, sulphur—Cu <sub>2</sub> S Copper, sulphur Copper, iron, sulphur Copper, iron, sulphur

Of these ores, copper pyrites (or yellow copper ore) is the most abundant, and probably copper glance is next in importance. Copper is also found in the metallic state in several parts of the world, the Lake Superior mines being among the best known. Copper at the present time is extracted from ores containing as low as 10 per cent. of the metal.

**Preparation of Copper.**—The method by which the copper is extracted from the ores will vary according to the ore treated. Thus, where the ore contains no sul-

<sup>\*</sup> Huntingdon and Macmillan.

phur—namely, oxides and carbonates—copper is obtained by the simple process of smelting the ore in a blast-furnace with coal or coke. Where mixed ores, especially when with sulphides, are present, the processes become more complex, of which the following is given briefly:

The Welsh Process for copper-smelting generally consists of six stages, the ores containing on an average

13 per cent. copper and 30 per cent. iron.

I. The ore is roasted or calcined at a dull red heat for twelve hours, to expel arsenic and part of the sulphur and partly oxidize the metals present. A reverberatory furnace is used, and the ore is broken into rough pieces.

2. The roasted or calcined ore is melted. Copper oxides present react upon a portion of the ferrous sulphide, forming cuprous sulphide and ferrous oxide. The ferrous oxide is carried off in the slag (formed from the silicates present in the ores or from the slag of the fourth process), leaving what is known as coarse metal, containing about 35 per cent. copper. By pouring this coarse metal into water it is granulated and prepared for the third stage.

3. The coarse metal is roasted, to convert more of the remaining sulphide of iron into oxide. The roasting is generally carried on for twenty-four hours, the

coarse metal being kept at a dull red heat.

4. Coarse metal from the third stage is melted with some of the slag from the sixth stage. Most of the remaining iron is carried off in the slag, leaving behind a regulus of copper, known as *fine* or *white metal*, containing from 60 to 75 per cent. of the metal as cuprous sulphide.

5. The fine metal is roasted from twelve to thirtysix hours to drive off more sulphur; part of the cuprous sulphide is converted to cuprous oxide, and the remaining ferrous sulphide to ferrous oxide. The copper after this roasting is known as *blister copper*, so called from

its appearance.

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6. The Refining Process.—The copper from the fifth stage is melted upon the hearth of a reverberatory furnace in an oxidizing atmosphere. Iron, arsenic, lead, etc., if present, are first to oxidize, the sulphides passing off as sulphurous acid, the oxides volatilizing or combining with the siliceous lining of the surface to form a slag. The copper itself then begins to oxidize, this oxide reacting upon any sulphide present, with the evolution of sulphur dioxide and the reduction of copper. The metal is now covered with a layer of wood charcoal or anthracite, and stirred with a pole of young wood (birch usually), this stirring being known as poling. which still further reduces any copper oxide present. The poling is continued until samples show the copper with a close grain, a silky fracture, malleable, and of a light red colour.

Blast - Furnace Process. — Blast-furnaces are largely employed to produce a crude metallic copper, known as black copper, direct from oxidized ores of copper, but more frequently to concentrate the copper in matts from which it may afterwards be recovered. The furnace charge generally consists of about 30 per cent. of copper, with balance of silica, sulphur, and iron, from the slag of a previous smelting. The copper is raised by this process to about 50 per cent., and the Bessemer or Welsh process, or some modification, is employed for the refining.

Bessemer Process for Copper Matts.—Converter very similar to that employed for steel, only twyers are arranged so that the air impinges just below the surface of the metallic matt. Charge consists of matts containing between 50 and 60 per cent. copper. As in the process for steel, the converter is heated, and receives the charge in the molten state. The blast is turned on, and, as the reduction proceeds, the slag containing most of the oxidized impurities is canted off. The reaction is not so violent as with steel, the flames are not markedly vivid, and the end of the process is reached when the

little sparks of copper given off from the fused charge are seen to rebound from the sides of the converter. It is claimed that a 99 per cent. copper can be produced

in this way.

Electrolytic Refining of Copper.—This process is chiefly employed for refining copper, or for extracting copper when gold and silver are combined. The sulphate or chloride of copper is the solution or electrolyte. If copper regulus is used, it is cast into slabs, which are suspended in a row and connected with the positive pole. Between each slab is hung a thin sheet of copper, each connected with the negative pole. It is upon these thin sheets that the fine copper deposits. Or the first slab or plate is connected with the positive pole alone, and the negative a slab of pure copper. By this means each copper slab after the first acts as cathode to the slab behind it, and anode to that in front, the copper being deposited from plate to plate until all is dissolved.

Such metals as platinum, gold, silver, lead, and slag, are not dissolved in the solution, and are left as a slimy deposit on the anode. The electro-motive force is usually about 0.3 volt between each pair of plates placed in series, and the last plate, being of pure copper, conducts the current back to the positive pole of the dynamo. Another wet process consists in depositing copper from bluestone, the crude commercial sulphate. The sulphate is brought to solution, and the copper reduced to the metallic state by means of zinc or iron plates suspended in the solution. The copper thus reduced is not chemically pure, and has to be washed in dilute sulphuric acid. (See Preparation of Copper Amalgam.)

**Properties of Copper.**—The melting-point of copper is 1,084° C. if melted under carbon, but 1,063° C. if melted in contact with air or oxygen. The specific gravity of freshly cast pure copper is 8.82, which can be increased to 8.90 by rolling. In colour copper is light red, and exhibits a salmon colour and a fine silky structure or

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fracture after rolling. Copper on solidifying presents a vesicular structure, by which the density of the metal is greatly diminished. This may be accounted for by the readiness with which copper occludes oxygen when in the fused state, and the effort of the enclosed gas to escape as the metal solidifies is probably the cause of the cavities or spaces. These are removed by hammering or rolling, bringing the molecular structure into closer apposition; hence the increase of specific gravity. In casting, copper, silver, or tin are at times added in small quantities, together with charcoal and borax to improve the surface of the casting by lessening the occlusion. Copper ranks next to silver in its power of conducting heat and electricity, which property is powerfully influenced by impurities, such as antimony, arsenic, bismuth, and nickel. Silver and gold are among the best conductors, yet either of these alloyed with copper reduces the conductivity of the metal.

Copper expands on solidifying; is not volatilized at ordinary furnace temperatures, requiring the oxyhydrogen blowpipe to flame effect this. The metal oxidizes at ordinary temperatures, and very rapidly at a red heat. In moist air, in the presence of CO<sub>2</sub>, it becomes coated with green copper carbonate, or verdigris. Copper is passive to strong nitric acid, but diluted there is a violent reaction, and nitric oxide is evolved. Hot sulphuric acid, either strong or diluted, attacks the metal, sulphur dioxide is evolved, and copper sulphate formed. Iron and zinc deposit copper from solution. The metal is also deposited from solutions of the chloride and sulphate by electricity. It unites with oxygen in two proportions, forming

cuprous oxide (Cu<sub>2</sub>O) and cupric oxide (CuO).

Commercial copper generally contains traces of antimony, arsenic, bismuth, iron, tin, and sulphur. Lead is added to sheet copper to facilitate rolling. For electric installations and conducting purposes the purest forms are generally employed, and known as "best selected." The Lake Superior copper is among the purest grades for this purpose. The metal may be soldered with silver solder using borax as a flux. Weak sulphuric acid pickle may be used.

# Alloys of Copper.

Gold and Copper unite in all proportions, the chief use being to harden the gold, reduce the carat, and minimize the whitening effect of the silver in various carats. (See Gold).

Silver and Copper unite in all proportions, the action being similar to that of gold; the purity is reduced, the silver is hardened. Coin silver and silver for art purposes contain traces of copper, advantage being taken

of its hardening effect. (See also Silver.)

Platinum and Copper alloy only at a very high temperature. Copper is added to platinum only as a vehicle for adding other metals, such as gold in the gold and platinum alloys for bands, porcelain inlay matrices, etc. (See Alloys of Gold.) Platinum and copper alloys resemble gold in colour very closely, and also in their specific gravities.

Mercury and Copper amalgamate freely, provided the

copper is finely divided. (See Copper Amalgam.)

Zinc and Copper alloy readily, the alloy of these being

known as "brass."

Nickel and Copper alloy in all proportions, and alloys are employed in the manufacture of the different grades of nickel silver. (See Nickel.)

Tutenag contains 45.7 per cent. copper, 17.4 per cent.

nickel, and 36.9 per cent. zinc.

Electrum Metal contains 51.6 per cent. copper, 25.8 per cent. nickel, and 22.6 per cent. zinc, and may be

employed for the same purposes as nickel silver.

White Metal contains copper and zinc, the latter in excess—the greater the percentage of zinc, the whiter the alloy—and is chiefly used for art purposes.

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Brass.—An alloy of zinc and copper. Ordinary brass contains from 30 to 40 per cent. zinc, and can be rolled or hammered without fracture or tear, cold or hot; with zinc 60 to 70 per cent. yields an alloy brittle and unworkable. Sheet brass of a good quality contains copper 70 per cent., and zinc about 30 per cent., with a trace of lead to facilitate rolling. Brass for casting frequently contains 50 per cent. zinc, 3 per cent. tin and lead, 47 per cent. copper. Brass was formerly used to a certain extent as a die metal in metal-work, but its high melting-point, contraction of the casts, the marked tendency of the alloy to liquate, and the deterioration after several heatings, have led to its disuse. The resemblance between gold and many of the alloys of copper in respect to colour have led to the use of these for objects of art, and, in the case of aluminium bronze, as a base for dentures, crowns, etc. The following list of alloys will convey an idea of the trade names and the proportions of zinc employed:

Pinchbeck contains copper 90 per cent. and zinc

10 per cent.

Dutch metal contains copper 84.6 per cent. and zinc 15.6 per cent.

Muntz metal contains copper 60 to 64 per cent. and

zinc 36 to 40 per cent.

Mannheim gold contains copper 75 per cent. and zinc 25 per cent.

Mosaic gold contains copper 50 per cent. and zinc

50 per cent.

Aich's metal contains copper 60 per cent., iron 1.8 per

cent., and zinc 38.2 per cent.

Sterro metal contains copper 55 to 70 per cent., zinc 34 to 44 per cent., iron I to 2 per cent., tin I to 2 per cent.

**Bronzes.**—These alloys generally contain copper and tin.

Gun-metal contains copper 90 per cent. and tin 10 per cent.

Bell-metal contains copper 80 per cent. and tin 20 per cent.

Speculum metal contains copper 67 per cent. and tin

33 per cent.

Tin added to copper has a hardening effect, as witness speculum metal; but if in excess the alloy is first brittle, and if tin is further increased it becomes soft. An alloy of copper and tin containing 18 per cent. tin has a

tenacity of 17 tons per square inch.\*

Phosphor Bronze.—Phosphorus added to copper has a hardening effect, imparting toughness, hardness, and elasticity, and is present in bronzes generally. The phosphorus may be added when the copper is molten, in the form of the phosphide of tin (phosphor tin), or phosphide of copper (phosphor copper), the alloy generally containing from 0.25 to 3 per cent. phosphorus, and 5 to 15 per cent. tin, and the remainder copper.

Tin phosphide alloys perfectly with copper, forming a homogeneous alloy, which is added in small quantities to the copper for the sheathing of ships, to help to overcome the corrosion of the metal by the sea-water. Industrially it is used for bearings of machinery, on account of its wear-resisting properties. Its tenacity is almost-equal to mild steel, with the advantage that it

yields more before fracturing.

Arsenic added to copper in the proportion of I to IO yields a white malleable alloy, which is used for faces of watches, clocks, barometers, thermometers, etc., owing to its colour, hardness, and because it does not readily discolour in air.

Aluminium Bronze contains 90 to 95 per cent. copper and 5 to 10 per cent. aluminium. This yields an alloy which must be remelted several times before it becomes homogeneous. In colour it resembles 12 to 20 carat gold, the colour varying with the proportions of copper—a fact which has led to its use for base-plates, and in the dental hospitals for crowns, backings for pivots, regu-

<sup>\*</sup> Huntingdon and Macmillan.

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lating appliances, and almost any purpose to which gold can be applied. In sheet form it is not readily oxidized in air or when in the mouth. The melting-point is about 1,700° F.; specific gravity, 7.68. The 5 per cent. alloy is best for dental purposes, being more malleable, ductile, etc. It is easily swaged for base-plates, if the precaution be taken to anneal it almost at a white heat for a few seconds. Annealing at an ordinary dull red has no effect, and the swaging is apt to cause it to tear, especially in deep palates, ridges, etc. The alloy draws readily into wire, and makes a useful form of strengthener for lower dentures where rigidity is required. The wire is much increased in strength if hammered, and its colour and freedom from oxidation is not objectionable if it should show in the finished dentures. be soldered with 20 or 18 carat gold solder, but does not flux so readily as gold. In casting it shows marked contraction, and the formation of a heavy coating of oxides on the surface for cast plates tends to blunt the casts, and even impedes the metal flowing through the gates. The high temperature required to melt it is also against its use for this purpose. The best pickle for the bronze is dilute nitric acid—i.e., I of acid to 3 to 4 parts water.

Preparation of Aluminium Bronze.—This alloy is known under several trade names, each make differing slightly in composition. Dr. Percy was the first to make it. Sir W. Roberts-Austin gives its tensile strength at 100,000 to 120,000 pounds per square inch in sheet form, and in castings from 70,000 to 80,000 pounds per square inch. The copper is first melted, and then the aluminium added, using an ordinary well-tempered fireclay crucible of ample dimensions. The union of the metals is accompanied by a rapid rise in temperature, the mass being raised to a white heat. The molten alloy should be granulated by being run into water and remelted several times, to insure perfect homogeneity; otherwise the metal is liable to be very brittle. In some

commerical forms lead is present, and the proportion of copper is subject to considerable variation, the variation in the aluminium deciding the figures per cent. of the alloy—e.g., 95 copper, 5 aluminium, is a 5 per cent. alloy. Turner recommends the following solder:

. I	HARD SOLDER.	MEDIUM H	MEDIUM HARD SOLDER.			
	88.8 per cen		54.4 per cent.			
Silver	4.68 ,,	Silver	27.0 ,,			
Copper	6.44 ,,	Copper	18.6			

Victoria Metal.—This is the trade name of the alloy containing copper, nickel, and a trace of zinc, the copper being not less than 90 per cent. In colour the alloy resembles 12 to 15 carat gold, and may be soldered with 12 carat gold solder. In its physical properties it closely resembles aluminium bronze, is lighter yellow in colour, and solders more readily. In some salivas the alloy oxides considerably. Its use is confined to strengtheners, practice crowns in hospital practice, and apparatus for cases of malocclusion. The alloy pickles best in dilute nitric acid. Castings of this alloy for dentures are brittle, besides which the tendency towards oxidation shown by flat plate is accentuated after castings have been in the mouth a few months.

Copper or Sullivan Amalgam.—This is the only form in which copper is employed alone alloyed with mercury. The resulting amalgam has been long famous for its great edge strength, lack of contraction, and in its own place forms a most useful amalgam for restoring tooth substance loss through caries. It should always be confined to the posterior teeth, as it darkens through oxidation, the black stain usually permeating the dentinal tubules, unless the cavity walls have been sealed with a layer of oxyphosphate of zinc or other cement. It is readily inserted, and should be condensed with pluggers or burnishers to insure solidity, adaptation to the cavity walls, and to remove excess of mercury. The amalgam takes from four to five hours to harden,

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but even then it is unsafe, where large restorations have been made, to bring the force of mastication to bear upon it, as it is liable to alter in shape or fracture. Patients should be cautioned against the use of the filled tooth that day. (See Dental Amalgams.)

Making of Copper Amalgam—Dental Laboratory Method.—Chemically pure copper sulphate (bluestone) is dissolved in warm water to form a weak solution. The weaker the solution, the finer the grain of the finished amalgam. Sheet zinc or iron is suspended in the solution, when the copper is deposited. The clear water is poured off and the copper transferred to an earthenware mortar; dilute sulphuric acid is added, and the copper stirred vigorously with the pestle; fresh water and acid are added, and the copper washed until the addition of acid does not discolour the solution. It is then well washed with water to free it from acid, and thε mercury added in the proportions of 2 of mercury to I of copper by weight. A little nitrate of mercury may be added to assist in the amalgamation. The mercury and copper are rubbed together until the mercury is evenly distributed, a little dilute sulphuric acid added again, the amalgam washed in hot water, dried, and the surplus mercury expressed through chamois leather. amalgam is then pressed into small button-shaped moulds, and allowed to harden. The amalgam on being heated becomes quite plastic, and may be resoftened without injury to its properties, provided that the hear is not sufficient to volatilize the mercury. It is sufficient if it be heated in an old iron spoon until mercury beads appear on the surface.

#### CHAPTER X

### METALLURGY OF GOLD

Symbol, Au. Atomic weight, 19720. Specific gravity, 19:30. Melting-point, 1,064° C.

Occurrence.—Gold is found almost exclusively in the native condition, chiefly in quartz, veins, and as nuggets in alluvial deposits, these deposits being formed by the disintegration of auriferous rocks. It is seldom found pure, being almost invariably alloyed or combined with traces of silver; it also occurs in the ores of silver, copper pyrites, iron pyrites, and many of the lead ores. It is found, too, combined with the rarer metals tellurium, platinum, and palladium, the traces of these metals generally being small. Combined with tellurium, gold occurs in varying quantities; thus,

Calaverite, AuTe, contains 40 per cent. gold.

Sylvanite, or graphic tellurium, (AuAg)Te<sub>2</sub>, contains 24 per cent. gold.

Nagyagite, or black tellurium, (PbAu)(TeS), contains

5 to 9 per cent. gold.

White tellurium, (AuAgPb).(TeSb)<sub>3</sub>, and Petzite, Ag<sub>2</sub>Te<sub>2</sub>Au<sub>2</sub>Te, also contain sufficient gold to repay treatment.

**Preparation of Gold.**—The treatment of ores for the extraction of gold is determined by the form in which the metal occurs, and other metals combined with it. The processes may be classified as under:

1. Extraction of gold by simple washing, or by dressing

gold-bearing sand, gravel, etc.

2. Extraction of gold by dry process—i.e., by concentrating the gold in the ore in a gold and lead alloy, or gold, silver, and lead alloy, and recovering the gold by cupellation.

3. Extraction of gold by wet process—i.e., by extract-

ing the gold from aqueous solutions.

4. Extraction of gold by combination of wet and dry processes, such as—

(a) By obtaining the gold as an alloy of gold and

mercury (amalgamation).

(b) By obtaining the gold as an alloy of gold and silver, or gold, silver, and copper, and dissolving the silver and copper.

5. Extraction of gold by electrolysis—i.e., by obtaining the gold as a gold-silver or gold-silver-copper alloy, and parting these metals from the gold by means of electrolysis.

I. Extraction of Gold by Simple Washing.—This process is only applicable to gold-bearing soils and alluvial deposits. The pan and cradle treatment of the early miner has disappeared. The modern sluice consists of a series of boxes or troughs 16 to 21 inches wide, and 9 to 12 inches deep. Each box is about 12 feet in length, the series extending several hundred vards in many mines. Water is allowed to flow through the sluice, which is inclined so as to keep up a steady flow. The gold-bearing soil is shovelled in at the head of the sluice, and, being caught in the water, is carried along. The earthy matter is broken up, and sets of short transverse wooden ridges catch the pebbles, and help to break up pieces of clay, etc. The gold, as it becomes free of the earthy matter, sinks, and is collected in a series of pockets let into the bed of the sluice; there it is caught in mercury, from which it is afterwards freed by heat. The pan and cradle process formerly employed entailed a loss as great as 50 per cent. at times; with the modern sluice the loss is very trifling.

Amalgamation Process.—When the ore is present in quartz form, and the gold present in paying quantities,

and provided the ore is one of the variety known as "free-milling" ores, or is one that will yield its gold readily to mercury, the quartz is crushed to powder in the mills or stamps, as described under the MacArthur-Forrest Process. The powdered quartz is mixed with water, and allowed to flow slowly over copper plates heavily coated with mercury. Those plates are ridged in places to obstruct the even flow, and are caused to vibrate to bring the finely divided gold down into contact with the mercury. The mercury absorbs the gold from the water, and the gold is recovered by distilling the mercury, which is recovered by condensing the vapours; the gold is then melted to ignots. The residue, or "tailings," from this process is generally treated by the cyanide process. There are many modifications of

this process.

Extraction of Gold by Wet Processes—The MacArthur-Forrest or Cyanide Process.—This process depends upon the solvent action of potassium cyanide on gold, and is especially adapted to such ores as yield their gold readily to mercury, such as free-milling ores, and to the tailings from the Amalgamation process. When quartz is under treatment, the first step is to reduce the stone to powder by some form of crushing machine. The crushing is seldom carried beyond the point when the powder will pass through a mesh of thirty to the linear inch, as if it is finer than this the gold is apt to be carried off in the scum or to remain in suspension. Where the quartz has been previously treated by the amalgamation process, however, it may be crushed as fine as sixty to the inch, the modern tube mill being employed. This powder in South African mines is soaked, or "leached," in potassium cyanide solution for three or four days for fine ores, and up to fourteen for coarse ores, the quantity of potassium cyanide used being from 0.35 to 0.6 pound per ton of ground ore or tailings. The ore is passed through several tanks containing the solution, until all the gold has been dissolved; the solution is then transferred to a series of long troughs, averaging about 24 feet long, 3 feet wide, and from 2 to  $2\frac{1}{2}$  feet deep. These troughs are subdivided, each compartment containing freshly cut zinc covered with wire mesh, with four holes to the inch. The action may be expressed theoretically thus,

# $2KAuCy_2 + Zn = KZnCy_4 + Au_2$

although more zinc has to be used in practice. The gold is deposited as a black slime, the zinc is dissolved with suitable acids, and the gold melted and run into ingots.

Extraction of Gold by Dry Processes—(I) By concentrating the Gold in Lead.—The ore is melted in a reverberatory furnace, and lead, either as galena, litharge, or lead slag, or any refuse containing lead, is charged into the furnace with gold-bearing ore. The lead acts in much the same way as mercury—that is, it collects any gold and silver present by reason of its affinity for them, and the gold and silver are afterwards separated by cupellation.

(2) By using Iron and Lime.—This process is employed for poor ores. The ores are roasted in air, and mixed with lime, when any metallic sulphides present are converted into oxides. The charge is melted in a blastfurnace, when the quartz of the ore and the lime combine to form a slag, beneath which the gold, with any silver and iron sulphide present, collects. These metals are treated by one of the "parting" processes to be described.

Electrolytic Deposition from the Auro-Cyanide Solution—(3) Siemens and Halske Process.—Electricity has been emlpoyed with success to displace zinc for the above purpose. Lead cathodes are used, and iron anodes; the gold is deposited on the lead cathodes, which are cupelled for the recovery of the gold. The current is low, being around 7 volts. There are several modifications of the above processes, such as the substitution of

potassium bromide for the cyanide, but the descriptions give the principles governing the processes in general.

Extracting Gold by Combination of Dry and Wet Processes—Chlorination Process.—In this process advantage is taken of the readiness with which gold combines with chlorine to form auric chloride. The ore treated by this process contains the gold in close intimacy with other metals, such as pyrites ore. The ore is roasted in a reverberatory furnace to drive off as much volatile matter as possible, and to render it more porous. It is then withdrawn, moistened, placed in tubs, and exposed to the action of chlorine gas. The gold and iron present are converted to chlorides, which, being soluble, are washed out with water, and the gold deposited by sulphuretted hydrogen being passed through the solution. Ferrous sulphate is said to give even better results than the gas for the deposition of the gold, the gold coming down in a purer condition.

The processes included under group No. 5 will be found detailed under the smelting process given, in the parting or refining process to be given, and in the Siemens

and Halske electrolytic process.

Treatment of Tellurium Gold Ores.—The ores are boiled with strong sulphuric acid, dissolving the tellurium and any lead, zinc, copper, and part of the silver, present, and leaving the gold and silica as a residue. The gold is then treated by cupellation. The tellurium solution is evaporated to a syrup, soaked in weak hydrochloric acid, and any gold or silver present is deposited and removed. The tellurium is deposited with liquid sulphur dioxide in the elemental state.

Parting or Refining of Gold.—The gold as produced by the processes given is seldom, if ever, pure; and the series of processes necessary to obtain the gold in the pure state, and to separate it from such valuable metals as platinum, silver, etc., is referred to as the parting or refining of gold. The treatment which the gold receives is governed by the metals present. The processes may be divided into three classes:

1. Dry methods, in which litharge, sulphur, sulphide of antimony, chlorine, or certain cement powders consisting of brick-dust, NaCl<sub>2</sub>, are the agents.

2. Wet methods, where nitric or sulphuric acids are

used to effect the separation.

3. The electrolytic method depends upon the fact that, when solutions containing gold and silver are electrolyzed, the gold remains at the anode, while the silver passes to the cathode, the electrolyte being an acidulated solution of silver nitrate.

Dry Method of Parting Gold-Miller's Process.-The gold is enclosed in fire-clay crucibles provided with well-fitting covers. It is covered with borax and lids luted to their places. The crucibles with the gold are placed within a second, and sometimes a third, crucible, with a layer of borax between each to prevent the gold passing into the body of the crucibles. The crucibles may also be treated by dipping into a solution of borax, drying, and heating to a high temperature before use. This renders them impervious to the precious metals or Each is provided with a luted cover, their chlorides. and into the cover of the crucible containing the gold is led a clay pipe, to convey chlorine gas as soon as the gold has melted. The gold absorbs the chlorine first as quickly as it enters; the metals present are converted into their respective chlorides, while volatile metals are given off as the temperature is increased. The vapours given off are at first white, and, when the process is complete, of an orange colour. The gold collects at the bottom of the crucible commercially pure, while the silver is present as the chloride. Miller fused the chloride with a little potassium carbonate. This reduces a small quantity of the silver, which, again, in separating from the rest of the chloride carries with it any gold present. The silver, either as the chloride or metallic silver, may

be dissolved in sulphuric acid, the gold removed, and the silver deposited from the solution by iron plates, etc.

Cementation Process.—The powder used consists of I part common salt to 2 parts brick-dust. The gold is laid in layers in crucibles made of porous clay, each layer being separated by some of the cement powder. The crucible and its contents are heated over wooden fires for twenty-four to thirty-six hours, and kept at a bright red heat. A large quantity of water is given off by the wood during combustion, which, entering the crucible, brings the salt, silica, and water, into combination at a red heat. The sodium of the salt is taken up by the oxygen from the water, and combines with the silica, forming sodium silicate. The chlorine of the salt takes up the hydrogen of the water to form hydrochloric acid. This acid, attacking the silver, forms silver chloride, which passes into the sides of the crucible. This process, repeated several times, yields a commercially pure gold.

Parting of Gold by using Sulphide of Antimony.—The process depends upon the fact that, if an alloy containing silver and gold be melted with sulphide of antimony, the silver combines with the sulphur, and the gold with the antimony. The alloy must contain at least 50 per cent. of gold, and the process must be repeated several times to insure complete parting. The antimony is driven off by heat, and the silver separated by being melted with lead or iron. Any silver still

present in the gold is removed by nitric acid.\*

Nitric and Sulphuric Acid Process.—The use of these acids is based upon the power which they have of converting silver and copper into their nitrates and sulphates, if employed as hot concentrated solutions, and upon the fact that they have no action upon gold. The metal to be treated is either in fine granules or thin sheets, and the hot acid added until all chemical action ceases—a sign that the silver and copper present are

<sup>\*</sup> Schnabel and Louis, vol. i.

dissolved. The liquid is decanted, and the gold as the residue is melted and cast into ingots.

Electrolytic Parting.—Several processes have been proposed at various times, but they have nearly all proved ineffective in use.

At the U.S. Mint, San Francisco, an improved

Wohlwill process is used.

The anodes are of gold bullion containing about 90 per cent. gold, and not more than 7 per cent. silver. The cathodes are of pure gold strip 0.012 inch thick. The electrolyte is a solution of gold chloride containing 60 to 70 grammes of gold per litre, and from 10 to 12 per cent. free hydrochloric acid. The current is a direct one of 15 volts, and passes through the fourteen cells of each set in series. The total current is 180 ampères. The anodes are dissolved in the electrolyte, and refined gold is deposited on the cathodes in a firmly coherent form. All the metals in the anodes go into solution except silver and some lead.

When the cathodes in a set of cells weigh about 10 pounds, they are removed and used as anodes in a second set of cells. By this redeposition a product of

about 999.7 fine is obtained.

As compared with the sulphuric acid process, it is more expensive, requires more care and attention in carrying it out, and the losses are likely to be greater in carrying it out on account of having gold in solution in the electrolyte. The advantages of the process are—the gold obtained is purer, all the platinum metals are saved, and there is no nuisance from acid fumes.

Preparation of Chemically Pure Gold.—The gold obtained by the ordinary parting processes just described averages from about 996 to 999 parts pure in the 1,000. As it is essential that the gold used for filling purposes be as pure as possible, that obtained by the above processes is generally best adapted to the purpose. The gold is dissolved in nitro-hydrochloric acid (aqua regia, a mixture of 1 part nitric to 2 parts

of hydrochloric acid). To this solution of gold chloride are added potassium chloride and alcohol, which deposit any platinum present. The platinum is recovered, and the solution then diluted until there is  $\mathbf{I}$  gallon of water for every  $\frac{1}{2}$  ounce of gold solution. Any silver present will combine with the potassium chloride, and be deposited as silver chloride.

This process generally occupies a few days, as the silver, by reason of its strong affinity for gold, separates out very slowly. Oxalic acid, ferrous sulphate, stannous chloride, or a stream of sulphuretted hydrogen, is added

to the solution, and the gold deposited.

The character of the deposited gold is very much influenced by the reagent used, and by the strength of the solution. Oxalic acid deposits the gold as a spongelike mass if used in diluted solution, and as crystals or leafy foil if used in strong solution. Ferrous sulphate deposits gold more granular than otherwise, the gold having a brown colour. Gum-arabic or sugar, if added to diluted gold solution and heated, deposits the gold as shreds, oxalic acid being formed by the decomposing of the gum-arabic or sugar. The electrolytic deposition of gold has already been described. Ferrous sulphate seems to be most favoured of the reagents in the use for preparing dental golds.

Properties of Gold.—As seen in the mass gold is the only yellow metal. When freshly precipitated, the colour, as has been said, varies with the reagent used. Gold when pure is almost as soft as lead, and can be welded in the cold state. Annealing tends to toughen the metal, but increases its ductility and tenacity, and renders it more malleable and cohesive. The term "cohesive" as applied to gold is somewhat analogous to that of "weldability" as applied to iron and other metals. If two pieces of gold-foil be annealed and brought together with a light flip or pressure, it will be found impossible to separate them. Under the glass or microscope it is seen that this cohesion is very inti-

mate. Advantage is taken of this property in building up contours on fillings, the cohesion enabling the operator to build on gold to the metal already in place after the restoration has been carried beyond the walls of the cavity. Pure gold inserted thoroughly into a cavity should not scale on the surface when exposed to the force of mastication, nor disclose any tendency to friability, change of shape, or discoloration.

Gold is more malleable and ductile than silver, leaves of gold having been rolled to  $\frac{1}{282000}$  inch, silver only to  $\frac{1}{10000}$  inch. Taken at  $\frac{1}{282000}$  inch, 56 square inches of this foil only weigh I grain (Greenwood). As an example of its ductility, I grain of gold has been drawn

into wire form to 500 feet (Percy).

Pure gold is greatly affected by the presence of impurities, even small traces of lead, antimony, platinum, iridium, or arsenic, having a most powerful effect on the malleability, ductility, tenacity, and cohesiveness. As a conductor of heat and electricity, gold ranks next to silver. This property of conductivity is one which demands attention when the metal is being inserted within reasonable distance of living pulp tissue. Frequently the cavity is lined, and the pulp protected by a lining of non-conducting oxyphosphate or oxysulphate of zinc cement. Pure gold either at ordinary temperatures or strongly heated is not affected by the atmosphere. Sulphuretted hydrogen does not affect the metal at ordinary temperatures, but double sulphides of gold and alkali metals are formed by fusing gold with an alkaline sulphide. Chlorine readily attacks the metal forming the chloride. Gold is dissolved by any reagent which liberates chlorine, which accounts for the solvent action of aqua regia. Oxalic acid precipitates gold from solution; so also arsenious acid, stannous and antimony chloride, arseniuretted and antimoniuretted hydrogen, sulphur, sulphur dioxide, and the ferrous salts. Gold is not acted upon by nitric, hydrochloric, sulphuric, or any single acid, except the selenic.

Gold for Filling Purposes.—The gold employed for filling purposes is nearly always pure, seldom being lower than 999.5 fine. It is employed in several forms —as cubes or cylinders, made from very thin foil rolled into coils, and cut to the different sizes; as foils of various thicknesses, the number of the foil generally denoting the number of grains in the sheet. For general work, the number of thickness ranges from 30 grains to 60 grains per sheet. Cubes, cylinders, and foils, are prepared under two classes—the cohesive and non-cohesive. The advocates of non-cohesive gold claim for its use greater softness in working, insuring a more accurate adaptation to the cavity walls, and greater hardness to the completed filling. Its use is usually confined to simple cavities—that is, cavities with all four walls standing. The non-cohesion of the separate pieces is against its use in compound cavities, especially where much contouring is necessary. It is not perfectly understood how non-cohesive golds are prepared, as all forms of pure gold without special treatment are cohesive after annealing. Gold, however, may be rendered noncohesive by the following:

1. By immersion in a metallic salt solution, such as

ferrous sulphate.

2. By the deposition of finely divided carbon on the surface.

3. By special mechanical treatment during the rolling and beating.

4. By forcing the gold to occlude certain gases.

Many of the so-called "non-cohesive" golds, as foil and cylinders, are only non-cohesive until they are annealed, when they lose this property, coating the gold with sulphuric ether and igniting being sufficient for the conversion\*; others, again, remain non-cohesive after repeated annealings. Moisture, grease, dust, and even humidity of the atmosphere, all tend to reduce cohesiveness in gold. The annealing process should be

<sup>\*</sup> Herbst, on "Gold Foils."

carried out carefully. The practice of exposing the gold to the naked flame of the commercial quality of methylated spirits reduces the cohesiveness, prevents equality of annealing, and causes scaling, friability, etc. The sheets of mica supplied for the purpose work efficiently, as do many of the electric annealers. The lamp with absolute alcohol flame is advocated by some operators for annealing heavy foils. Unless where the alloy of gold and platinum is used, the annealing should not be carried beyond a cherry-red heat. The alloy, however, behaves best with a bright-red heat, and should be kept at this temperature for a few seconds. Matt golds, or gold deposited as crystals, shreds, and leafy deposits, are generally of the cohesive type. They may be had as cubes, blocks, or strips, and are deposited, from a solution of pure gold by means of various reagents. Thus—

I. Ferrous sulphate deposits gold as a light brown-

coloured powder.

2. Oxalic acid deposits gold, according to the strength of the solution, from a spongy and leafy deposit to a

brown powder.

3. Electricity is now employed, the cathode being platinum, and the anode being a plate of pure gold. The deposit is in the crystalline form, as supplied in matts. The other reagents are seldom employed for

depositing gold as matt for dental purposes.

Matt gold is frequently employed for basing large cavities, as it is readily inserted, resembling amalgam in many of its working properties. By some operators it is carried to the surface of the cavity; others, again, prefer to finish the filling with foil or cylinders, as these, they consider, give a denser surface, and are less liable to change of shape. The gold supplied in the various forms alloyed with platinum, while giving a much tougher surface, is discarded by many on account of its colour. As foil, it appears very light in colour, but when highly polished looks almost black. In matt form, when inserted, it resembles a low-carat gold, being

very red in hue. Many of these alloys contain, besides gold and platinum, traces of silver and copper. Annealing renders them cohesive, but they never reach the kidlike softness of most of the pure golds. In foil form they are admirably suited for making matrices for fused porcelain inlays, etc., the alloy being tougher, more elastic, and bearing more burnishing without thinning or tearing. If annealed frequently, it can be made to spring from the cavity without change of shape. The melting-point is also higher than that of pure gold.

# Alloys of Gold.

Pure gold is too soft and too expensive for most industrial and dental purposes. When chemically pure, it is known by jewellers as "fine" gold, and described as 1,000 fine, or of 24 carat fineness. The term "carat" is difficult to trace, some ascribing it to the Greek word keration, a seed or bean formerly used as a weight. Now it is regarded as simply expressing a unit, whether an ounce, pound, or pennyweight, each unit being divisible into twenty-four parts. Each part of an alloy or other metal present will reduce the carat fineness. Thus, if there be 22 parts gold, I of silver, and I of copper, we have the 24 carats reduced by 2, yielding 22 carat gold, the figure of the carat always expressing the parts of pure gold present. Gold of 22 carats is known as "standard gold," a term used by goldsmiths, and when it is said that a gold is so many carats better or worse than "standard gold," it means higher or lower than 22 carat gold. Alloving of gold generally has in view the cheapening of the production, the hardening of the metal, and the lowering of the fusing-point. Silver and copper are the two metals mostly employed for this purpose, the silver overcoming to a great extent the reddening effect of copper.

Gold Plate.—In the laboratory pure gold is mostly employed in cases of continuous gum work and as a

solder for bridge work. In such cases the foundations or bases are of platinum or iridio-platinum, the pure gold being employed as a solder when high fusing bodies and enamels are employed, because the pure metal will not discolour the porcelain or delicate gum tints by oxidation during firing. Also as the outer shell in seamless and two-part crowns.

Crown Gold.—Plate for crowns is usually of 22 carat gold, which is tougher and harder than the pure metal, does not discolour in the mouth, and, being easily bent, is readily and accurately adjusted. British gold coin is employed for this purpose, but the redness imparted by the addition of copper to increase hardness is against its use. Australian gold coins rolled to No. 4 British gauge, being lighter in colour, give good results. Professor C. L. Goddard gives the following as having the colour of pure gold and of 21.6 carat:

No	o. I.		No	0. 2.	
Pure gold		90 parts.	Coin gold		50 parts.
,, silver		5 ,,	Pure ,,		45 ,,
" copper		5 ,, .	,, silver	• •	5 ,,

Crown gold is generally of No. 4 British gauge, the solder being 20 carat, or No. 00, for the seam of the ferrule, and 18 carat solder, or No. 1, and chips of 18 carat gold for loading the top where the crown is made in two pieces. When seamless crowns are made, the top is loaded with No. 1 gold solder. Many prefer to make the ferrule with pure gold, British coin gold, or from one of the above formulæ, and the top from such as the following, the platinum imparting greater hardness:

Pure gold	 • • .		22 dwts.
,, silver	 	• •	18 grs.
,, copper	 		I dwt.
Platinum	 		6 grs.

Gold Plate for Bases.—The gold for these seldom exceeds 18 or 20 carat, the most common being 18 carat for general purposes, and of 7 or 8 English gauge thick-

ness. In the mouth these carats do not readily discolour, are easily kept clean, and do not irritate even the most sensitive mucous membrane. Silver and copper are the two metals used to reduce the carat.

# Alloys of Gold used in Dentistry as Bases, Clasps, and Wires.

### 20 CARAT GOLD FOR BASE-PLATES.\*

Pure gold		20 dwts.	American coin gold	20 dwts.
,, silver		2 ,,	Pure silver	20 grs.
,, copper	·	2 ,,	,, copper	18 ,,

#### 18 CARAT GOLD FOR BASE-PLATES.\*

Pure gold	 18 dwts.	Pure gold	 18 dwts.
,, silver	 2 ,,	,, silver	 3 ,,
,, copper	 4 ,,	,, copper	 3 ,,

#### 16 CARAT GOLD FOR BASE-PLATES.\*

Pure gold	1	6 dwts.	Pure gold		II dwts.
,, copper		4 ,,			3 dwts. 6 grs.
,, silver		4 ,,	,, copper	r	2 dwts. 6 grs.

### 20 CARAT PLATINIZED GOLD FOR CLASPS AND WIRES.†

Pure gold	 20 dwts.	Coin gold	 20 dwts.
,, copper	 2 ,,	Pure copper	 8 grs.
,, silver	 ı dwt.	,, silver	 10 ,,
,, platinum	 I .,	Platinum	 IO ,,

# 18 CARAT PLATINIZED GOLD FOR CLASPS AND WIRES.†

Pure gold	 18 dwts.	Pure gold		18 dwts.
,, silver	 4	" copper		3
,, copper	 ı dwt.	,, silver		2 ,,
Platinum	 I	, platinun	1	ı dwt.

	PLATIN	IZED	GOLD FOR	CLASPS	AND W	VIRES.	
	17 C	arat.			16	Carat.	
Pure	gold		17 dwts.	Pure	gold		24 dwts.
,,	copper	• •	4 ,,		copper		2 ,,
,,	silver	* .	2 ,,		silver	• •	ı dwt.
2.2	platinum		ı dwt.		platinui	m	Ι,,

<sup>\*</sup> Richardson's "Mechanical Dentistry."

<sup>†</sup> Essig and Koenig.

I dwt.

It is a general practice, when using platinized gold for making flat plate, to displace half the copper with platinum, and for clasps, where the hardening effect of the copper is necessary, to displace half the silver with

platinum.

Gold Solders.—Solders generally range from 20 carat down to 12 carat, although many are found much lower. Below 12 carat they oxidize rapidly, and the purpose is to solder with as high a grade as the base, clasp, etc., will permit. The solder must always be lower in carat and fusing-point. Professor Goddard gives a simple method of producing a suitable solder. Take 5 parts of the gold plate itself, and add 1 part brass or silver solder. This produces a solder which flows freely. Zinc added to many gold solders has the effect of lowering the fusing-point, and causing the solder to flow better on becoming liquid.

Dorrance's alloy for reducing gold to solder gives good results, added in the proportion of 4 parts of the plate

to I part of the alloy:

copper

Brass

Copper Silver Zinc		••	••		6 parts. 2 ,, 4 ,,
		22 CARAT	Solder.		
Pure gold Brass					22 grs. 2 ,,
Pure gold Dorrance's allo	 y		Pure g	old ilver	5 dwts. 12 grs. 6 ,,
Coin gold Pure silver		18 CARAT 30 parts.	Coin g	old	19½ dwts.

copper

Brass

I part.

# 16 CARAT SOLDER.

	Pure gold 11 dwts. 12 grs.
,, silver 3 dwts 6 grs. ,, copper 2 ,, 6 ,,	,, silver 3 dwts. ,, copper 1 dwt. 12 grs. ,, zinc 12 grs.

# 15 CARAT SOLDER.

Pure gold		15 dwts.	Pure gold	 15 dwts.
,, copper		5 ,,	,, copper	 4 ,,
,, silver	• •	4	,, silver	 4 , ,,
			Brass	 ı dwt.

# 14 CARAT SOLDER.

Pure gold	 	14 dwts.
,, silver	 	
,, copper	 	3 dwts. 12 grs.
., zinc	 	I dwt. 12 grs.

# 12 CARAT SOLDERS.

Pure gold		12 dwts.	Standard gold		13 dwts.
" copper	• •	6',,	Pure silver		6 ,,
,, silver	• •		,, copper	• •	5 ,,
Brass		r dwt.			

# MELTING-POINTS OF VARIOUS CARATS OF GOLD (C. ASH AND SONS).

•	(0		551.5,.	F.°
Fine or pu	re gold			 1,980
22 carat				 1,800
20 carat				 1,760
18 carat				 1,700
17 carat p	latinized	band gold	d	 1,800
16 carat b	and gold			 1,640
16 carat				 1,620

# Melting-Points of Various Carat Gold Solders (C. Ash and Sons).

` '	F.°	C.°
22 carat, for use with fine gold	1,730	943
20 carat, for use with 22 carat gold	1,650	899
18 carat, for use with 20 and 18 carat gold	1,560	849
No. oo, for use with crown gold	1,620	882
No. 1, for use with 16 and over 16 carat gold	1,530	832
No. 2, for use with over 13 carat gold	1,480	804
No. 3, for general work and for dental alloy	1,430	777

The fineness of the several carats in common use is—

For 22 carat plate	 19.416 carat.	0.809 fine.
,, 20 ,, ,,	 17.496 ,,	0.729 ,,
,, 18 ,, ,,	 15.600 ,,	0.650 ,,
,, 16 ,, ,,	 13.656 ,,	0·569 ,, 0·490 ,,
., 14 ,, ,,	 11.760 ,,	0.490 ,,

Gold and Platinum.—Platinum added to gold imparts hardness and elasticity, but produces a paler colour. When over 5 per cent. is added, the alloy is much harder, more liable to fracture on swaging, and oxidizes more rapidly. In excess of the "content" 5 per cent., the alloy is acted upon by nitric acid. In foil form for filling purposes the amount of platinum seldom exceeds I or 2 per cent. These foils may be prepared by placing a thin foil of platinum over the gold early in the beating process, when the platinum is disseminated through the gold.\* In plate for clasps, wires, etc., from I to 3 per cent, added imparts greater strength and elasticity, an important property for clasps. The alloy is seldom used for base-plates, being too hard and elastic unless the platinum is kept very low in percentage. The two metals alloy readily, copper being employed as the medium to effect the alloving. Clasp gold with an inner lining of platinum is sometimes used where the tooth embraced has an amalgam filling coming in contact with the clasp; the platinum, it is held, being less affected by the mercury of the amalgam.

Gold and Silver.—Silver added to gold impairs the colour, increases the hardness without reducing malleability, and reduces the melting-point considerably. It is for these properties, hardness and reduction of the melting-point, that silver is employed. The metals alloy readily, although silver is seldom added to gold

alone. (See Silver and Gold.)

Gold and Copper.—Copper and gold unite freely, the copper diffusing itself through the gold very perfectly. The union of the metals is accompanied by a slight rise

<sup>\*</sup> Herbst.

of temperature, some writers holding that when 76 parts of pure gold and 24 parts of pure copper are melted together, a chemical combination ensues. Such an alloy is crystalline and brittle, and is never employed. Copper reddens the colour of gold, reduces the melting-point, increases hardness and toughness, but reduces the malleability and ductility. (See also Copper and Gold.)

Gold and Palladium.—Palladium added to gold, even in small quantities, renders the metal brittle and unworkable. The alloy is seldom prepared, and the two metals can be separated only with great difficulty.

Iridium has a similar effect.

Gold and Iron.—Essig mentions an alloy known as "blue gold," containing 75 per cent. iron and 25 per cent. gold. Many of the old bronzes contained traces of gold in their composition, the gold lending a beauty to the colour, besides lessening oxidation. The effects of such metals as tin and zinc, when present in gold alloys, are best studied under amalgams, as they are never added singly.

Lead present in gold, even to the extent of I part in I,000, renders the gold brittle. Antimony and bismuth

have a similar effect if added.

Calculations of Carat Fineness of Gold Alloys.

1. To find the carat of an alloy.

RULE I.—Multiply the weight of the gold present by the given carat, and divide by the combined weights of the metal of which the alloy is composed.

Example 1.—Gold, 6 parts of 24 carats; silver, 2 parts; copper, 1 part. Total, 9 parts. Find the carat of the alloy.

 $6 \times 24 = 144 \div 9 = 16$  carats.—Answer.

Example 2.—Gold, 24 parts of 22 carats; copper, 8; silver, 6. Total, 38 parts. Find the carat of the alloy.

 $24 \times 22 = 528 \div 38 = 13.9$  carats.—Answer.

RULE 2.—As the weight of the alloyed mass is to the weight of gold it contains, so is the carat of the latter to the carat of the former.

Example.—18 dwts. pure gold, 2 dwts. silver, 4 dwts. copper. Total, 24 parts. Find the carat of the alloy.

Gold Carat
Parts. present. given.

24 : 18 :: 24 = 18 carat.

2. To reduce the gold to a required carat.

RULE I.—Multiply the weight of the gold taken by its carat, and divide by the carat required. The quotient gives the weight of alloy to be made. Subtract from this the weight of gold used, and the difference is the weight of inferior metals to be added.

Example.—Reduce 4 ounces of 20 carat gold to 16 carats.

 $4 \times 20 = 80 \div 16 = 5$ . 5-4 (the total weight of the alloy) = I ounce alloy required.

RULE 2.—As the required carat is to the carat used, so is the weight of the mass used to the weight of the alloyed mass when reduced. The weight of the mass used subtracted from this gives the quantity of alloy required to effect the reduction.

Example.—Reduce 4 dwts. of 18 carat gold to 12 carat.

12 : 18 : 4 = 6 - 4 = 2 dwts. alloy required.

3. To raise the gold to a higher carat.

RULE I.—Multiply the weight of alloy used by the difference between its carat and that of the metal added, and divide by the difference between the carat of the metal to be added and that of the alloy required. Subtract the weight of the metal used, and the answer gives the amount of the gold required.

Example 1.—Raise 10 dwts. of 16 carat gold to

18 carat, using pure gold.

Multiply 10 by 8 (difference between 16 and 24), and divide by 6 (the difference between 18 and 24).

 $10 \times 8 = 80 \div 6 = 13\frac{1}{3}$  — 10 (the weight of the metal used). *Answer*:  $3\frac{1}{3}$  dwts. of pure gold required.

Example 2.—Raise II dwts. of 18 carat gold to 20 carat, using 22 carat gold.

 $II \times 4 \div 2 - II = II$  dwts. of 22 carat gold required.

Rule 2.—As the alloy in the required carat is to the alloy in the given carat, so is the weight of the alloyed gold used to the weight of the changed alloy required. Subtract the weight of the alloy used; answer gives the amount of gold required.

Example.—Raise 4 dwts. of 16 carat gold to 18 carat by adding 22 carat.

First subtract 16 from 22 = 6, then 18 from 22 = 4.

4:6::4=6 dwts. -4=2 dwts. of 22 carat gold required.

Treatment of Scrap Gold.—The presence of impurities exerts a powerful influence on the working properties of gold. Such metals as arsenic, antimony, lead, zinc, and iron, if present in small quantities, lessen malleability, ductility, and tenacity, and if present to any appreciable extent, make the gold brittle, friable, and unworkable. Dental gold is specially liable to become contaminated with such metals as platinum from porcelain teeth, etc., and with iridium as the iridio-platinum alloy; with traces of zinc from dies, lead from counter-dies, steel from broken fretsaws, dust from metal files, and traces of dental alloy. The greater portion of these may be readily removed by simply picking them from the gold before melting, but there frequently remain traces which can be eliminated only by special treatment. The

removal of such metals as platinum and iridium requires special care, as it is always attended with great difficulty, and often with loss of precious metals. Steel filings and broken saw-blades are readily removed by passing a good magnet into and over the scrap gold. The crucible used (plumbago) should be well tempered, well coated inside with borax, and raised to a red heat, so that the borax will glaze and prevent any of the gold passing into the body of the porous crucible. Ordinary scrap gold requires no further treatment than being brought to the melting-point, having plenty of borax added, being kept at a bright red heat for a few moments, and then poured into an ingot and rolled in the usual way.

Messrs. Fletcher of Warrington supply several useful appliances for the melting of gold and other metals, economy of heat being the governing principle. Their melting tray and ingot combined is especially useful where gold up to a few ounces is being treated. The gold can be poured from the crucible, free from molten borax, on to the fire-clay tray, and when it becomes thoroughly liquid the apparatus is tilted, and the gold run into the clean, warm, and well-oiled steel ingot mould. If, after rolling, the gold is found to be brittle even when well annealed, it should be further dealt with as brittle gold. The fracture should be carefully examined. If close in the grain and of a pale yellow colour, tin and lead are present; if dull brown, iron or some other foreign matter is the cause of the brittleness.

Treatment of Brittle Gold.—The crucible which is best suited for gold melting, as for dental work, for this purpose is prepared from plumbago (graphite), mixed with a binding material, such as Messrs. Morgan of Battersea list as their "Salamander" crucible. The crucible prepared from compressed carbon, made by the Carbon Crucible Syndicate, absorbs heat more rapidly, is more impervious when glazed, but for workroom purposes is more friable and less durable. The crucible is well rubbed on the inner surface with charcoal to prevent the

gold adhering to the surface, then heated gradually and coated with dry borax, or a saturated solution of borax in water, until the surface shows white. It is then placed in an inverted position in a good coke furnace, or one of Messrs. Fletcher Russell's, of Warrington, injector furnaces, and raised to a bright heat until the borax glazes. The use of too much borax both in glazing the crucible and in melting the metal should be carefully avoided, as loss of metal frequently occurs through the presence of excess of slag. The gold is then brought to the melting-point, and potassium nitrate added. The crucible, or the furnace containing it, should be placed in a strong upward chimney draught, when this reagent will help to oxidize such metals as lead, iron, steel, copper, silver, tin, zinc, and antimony. This process may be repeated several times, or the gold may be poured into a fresh, clean, and tempered crucible coated with borax and sal ammoniac (ammonium chloride), I part, with powdered charcoal, 2 parts, added. chlorine combines with most of the base metals present to form volatile chlorides, which either pass off or are caught in the borax slag. This latter process seems to be preferred by goldsmiths and jewellers.\* Mercuric chloride has been employed for this purpose, but the poisonous nature of its fumes render its use in ordinary dental laboratories inadvisable.

Where platinum is present in sufficient quantities to cause brittleness, the gold has to be subjected to one of

the "parting" processes already described.

Iridium is more difficult to remove. The gold is alloyed with three times its weight of silver; the iridium, by reason of its higher specific gravity, sinks, when most of the gold and silver may be poured off. The process may be repeated several times with what remains in the crucible; then the alloy is digested in sulphuric acid when the silver is dissolved, and the iridium is recovered as a deposit.

<sup>\* &</sup>quot;The Art of the Goldsmith and Jeweller," p. 57. 1911.

Treatment of Lemel and Sweep.—The sweepings from the dental operating-room and laboratory contain a large proportion of organic material. To extract the gold, bring the sweep to a dull red heat, which burns off most of the organic matter, and reduces it to ashes. These are mixed with the following: For every 50 parts of ashes by weight, 5 parts sodium carbonate, 5 parts borax, 2 parts potassium bitartrate (argols) or nitre, and 5 parts common salt. The ash is mixed with the sodium carbonate, borax, and nitre, covered with common salt, and raised to melting-point in a large crucible, and when all action of the flux has ceased the metal is poured into an ingot. The further treatment must be regulated by the behaviour of the gold when rolled. If brittle, the process already described is followed. In smelting works, where large quantities are treated, the ashes are charged into a reverberatory furnace, and lead added to concentrate any gold and silver. If silver is present in quantity, some iron is added to combine with any sulphur contained in the slag, and thus prevent the carrying off of the silver. The metals are separated by cupellation. The lemel (filings) are best treated separately, employing the same process as in the treatment of scrap gold, care being taken to use a crucible with a cover until the borax collects the filings in the slag.

**-Assaying of Gold.**—The assay process is divided into two divisions—the wet process of parting already dealt with, and the fire assay.

Fire Assaying.—This process is based upon the readiness with which gold and silver will combine with lead, and the power possessed by lead to decompose metallic salts. Silver chloride, for instance, if melted in presence of lead, will yield

## 2AgCl+Pb=2Ag+PbCl<sub>2</sub>,

which equation describes what has taken place. If volatile compounds, such as antimony, arsenic, mercury, etc., are present, the metal is subjected to a preliminary roasting at a temperature sufficiently high to volatilize or oxidize these. With the precious metals, the quantities of the metals assayed in each firing are divided into what are known as "assay tons," and generally marked "a.t." Each a.t. weighs 29.166 grammes, and as many of these "tons" may be treated as desired. With each charge the reducing agents must also be present in definite quantities; thus, for each a.t. of metals present there must be also I a.t. of litharge (lead oxide), 2 a.t. of soda ash, ½ a.t. of borax glass, and 3.5 grammes of crude potassium bitartrate (argols). Each charge is placed in a well-tempered crucible of ample dimensions. As the temperature rises the disturbance ceases, and when the metals have melted the charge is allowed to cool slowly. It is then withdrawn from the crucible, and the slag broken from the metal, which, being in the form of a lead button, is then cupelled or passed through the scorification process. The cupellation process is best adapted for assaying gold ores, whereas with silver ores the scorification followed by the cupellation process is of the greatest value.

Scorification Process.—In this process advantage is taken of the fact that, if silver be melted with lead in a current of air, the lead reduces and oxidizes any insoluble metallic salts present. "Test lead" or "lead shot" is used in place of litharge, 10 a.t. of test lead being added for each a.t. of silver ore present. The scorification dish or crucible is shallow, and of a finer texture than the ordinary fire-clay crucible. One-half of the lead is placed in the scorifier, then the silver, and the remainder of the lead added as a covering. The charge is kept molten for some time, borax being added from time to time, and the volatile compounds and reduced oxides are carried off in the current of air, generally established as an upward draught. These are generally seen rising as a thick, greasy vapour, and when this ceases, and the lead is seen clear and watery, the charge is poured off, and the slag broken free of the metal, which is next cupelled.

Cupellation Process.—The dish or cupel used in this process is round and thick, with a shallow concavity to receive the assay charge. The cupel is composed of bone-dust moistened with water and pressed into shape, care being taken not to produce a dish too dense, as this would retard the absorption of the oxidized lead. This process also depends upon the oxidizing effect of lead oxide upon the metals present, and on the fact that the lead oxide fuses, and is absorbed by the bone-ash of the cupel, carrying with it any base metals present, or is partly dispelled by oxidation.

The lead button being placed in the hollow of the cupel the latter is placed in a modified form of muffle furnace, provided with a mica panel for observation purposes, and the door closed. The heat is gradually increased until the charge is melted, care being taken to maintain the temperature as evenly as possible; cooling means loss of metal through some of it passing into the body of the cupel; and overheating, loss of metal by oxidation. As the process proceeds, it is noticed that the same thick vapour hovers over the charge, and that the bulk of metal is gradually lessening. a film of oxides appearing on the surface, and then quickly disappearing. When the last of the lead has disappeared into the cupel, the rest of the metal suddenly turns on its axis, and becomes covered by the most varied and beautiful tints, this change being referred to as "the brightening of the assay." The heat is now increased to expel any traces of lead present, and the cupel allowed to cool slowly. The metal remaining should contain the precious metals present, minus the other metals that were present as impurities. There is always a slight loss of silver, partly through oxidation, and partly through the lead carrying some of it off. The process takes from twenty to thirty minutes to complete, when the metals, such as gold, platinum, or silver, may be recovered by one of the parting processes already described. It has been found that there is not

complete separation of the gold and silver present unless the quantity of silver is at least thrice that of gold; so that, where doubt exists on this point, silver may be added even to excess. The process described refers generally to the assaying of alloys containing gold, silver, platinum, zinc, mercury, etc., such as are met with in dental amalgams; but where silver or gold alone is being assayed, the process is slightly modified. With large quantities of metals such as are treated at lead-works, where the lead contains paying quantities of silver, the process is modified by the substitution of larger vessels in the cupelling. In the German cupellation process, for example, cupels are large enough to receive charges of 25 tons of metals. Such processes are best studied

from text-books on lead, silver, and gold.

Assay for Hall-Marking.—The processes of cupellation and parting are adopted on a small scale for the assaying of gold alloys at the assay offices for the purpose of hallmarking. The test is carried out on a 5-grain sample taken from the alloy to be tested. The carat of the alloy is declared by the sender previous to the test, and as a rule a few grains of extra gold per ounce are added to insure the desired carat marking being attained. The 5 grains taken form one "assay quantity," and when a considerable bulk of metal is being tested several of these assay quantities may be taken. To each assay quantity fine silver is added to the extent of two and a half times the quantity of fine gold judged to be present in the alloy. The alloy and the fine silver are then wrapped in pure lead-foil, known as "assay lead," weighing sixteen times the weight of the alloy in the gold to be assayed. It is now placed on a cupel and passed through the cupellation process, when most of the copper is oxidized, leaving the gold and silver as a bead on the bottom of the vessel. The bead of gold and silver is then hammered and drawn into a narrow tongue under the rolls, and coiled into "cornets" and subjected to the nitric acid parting process. This dissolves out the silver, leaving a residue of fine gold, and from this residue the carat is derived. When greater exactness is desired, or when doubt is felt as to the result obtained, a "check assay" is carried out.

Check Assaying.—The check assay, or "trial plates," as they are sometimes called, are passed through the cupellation process at the same time as the alloy being tested to assure uniform condition. In this assay a quantity of pure gold equal to that present in the alloy is taken, the same addition of fine silver and assay lead being made. Check assays are of value by reason of the fact that gold is said to be slightly volatile at muffle furnace temperature, and there is a loss by absorption into the bone-ash body of the cupel. Also there may be a trace of copper left after the cupelling, and a little silver after the nitric acid parting. These causes may account for the "check" gold being heavier or lighter after being assayed. If heavier the increase is deducted from the weight of the gold being assayed with it, and if lighter the loss is added.

Assaying by Touchstone.—In assaying articles of jewellery, use is frequently made of what goldsmiths refer to as the "touchstone," a dark, smooth, and very hard stone of basaltic origin, or even of black slate, over which the article is drawn so as to leave a line of minute particles of the metal. The streak is then touched with nitric acid, with a trace of hydrochloric acid and water added, when such metals as copper and silver are dissolved. The streak is then compared for colour with a set of "touch needles" (a series of gold alloys of definite compositions), and from this comparison the carat of the article is found. Rose states that the assay by the touchstone or touch needles is best adapted for alloys below 18 carats, and that the gold present in an alloy can be determined correctly to 5 parts per 1,000.

Colouring of Gold.—This term refers to the process by which a film of pure gold is obtained on articles made from gold below the carat of fine gold, and which is

generally employed to improve the colour of the gold. The gold is heated over a Bunsen to a dull red heat, and plunged into nitric or sulphuric acid while hot. The acid dissolves out most of the silver and copper from the surface, leaving a layer of comparatively pure

gold.

There is also a dry process, in which the gold is immersed in a paste composed of common salt, 4 ounces; alum, 4 ounces; and saltpetre, 8 ounces. The action is similar. It is not usual to colour gold below 12 or 13 carats, as the lower the carat the greater the action of the acid, which, dissolving the silver and copper, leaves the surface irregular.

Electro-Gilding.—The solution or bath is of chloride of gold and potassium cyanide, the positive pole of pure gold, and the negative the article to be gilded suspended on a copper wire. The article to be gilded is made perfectly clean by immersion in a hot solution of caustic potash, and rubbed with a clean metal scratch-brush. The gilding bath is kept at between 160° and 212° F.; the larger the article, the higher the temperature required. The bath remains fairly constant owing to the gradual solution of the gold plate of the positive pole. The varieties of gilding apparatus used by the profession vary, the batteries developing a current of from 2 to 3 volts. When sufficient gold has been deposited, the article is withdrawn, washed, and polished.

Gold-Beating.—The pure gold is cast into ingots,  $\frac{3}{4}$  inch in width, each weighing from I ounce to 2 ounces. The hammer employed is heavy, with a circular and slightly convex face, 4 inches in diameter. The ingot is annealed and hammered on a steel anvil until it is  $\frac{1}{8}$  inch in thickness, when it is rolled out in ribbon form to  $\frac{1}{3000}$  inch. The metal is frequently annealed during the process to prevent fracture or tearing. The ribbon is now cut into I-inch squares, and placed in piles of 150, with a layer of specially toughened paper or vellum

dividing the layers. The pile is rolled into two wrappings of this paper or vellum, placed on a marble block or anvil, and hammered. The 1-inch squares are hammered until they are 4 inches, which are again cut to 1-inch squares, and piled as before, with a layer of "goldbeaters'-skin "between them. This "skin" is a membrane prepared from the peritoneal or serous coat of the intestines of the ox. These piles or "shoders" are again hammered until the required thinness is attained. Pure gold can be reduced much further than its alloys, and may be made to present a surface 650,000 times as large as it originally possessed.\* For dental foils, the gold of 1,000 fine is reduced as detailed, the number of the foil denoting the number of grains in a 4-inch square sheet; thus, No. 30 foil has 30 grains per 4-inch sheet, and so on. Herbst states that platinized goldfoils are prepared by superimposing a thin foil of platinum over the gold in the early stages of beating. By this means the two metals are closely welded and the platinum diffused.

**Purple of Cassius.**—This compound of gold, so called from its discoverer, Andreas Cassius, was first detailed in 1685, and largely employed at that time for imparting a beautiful ruby-red colour to glass for art purposes. It is used by dental porcelain manufacturers for imparting the gum tints to porcelains used in manufacturing gum-sections teeth and in continuous gum work. The exact composition of the compound is extremely uncertain. It is known to contain the oxide of tin and metallic gold, but the distribution of these in the compound is difficult to express. Bloxham gives it thus:

 $\mathrm{Au_2O.SnO_2} + \mathrm{SnO.SnO_2.4H_2O}.$ 

There are numerous ways of preparing the compound:

1. By adding a mixture of stannous and stannic chlorides to a solution of auric chloride, made as neutral as possible.

<sup>\*</sup> Huntingdon and Macmillan

2. By adding stannous chloride to a solution of ferric chloride until the yellow colour changes to a pale green; then add to a solution of auric chloride, when

the gold is precipitated.

3. By melting together  $2\frac{1}{2}$  parts gold with  $3\frac{1}{2}$  parts tin and 15 parts silver, the metal being fused under borax to prevent oxidation. The alloy is treated with nitric acid to dissolve out the silver, leaving the precipitate of a deep purple colour (Greenwood).

4. By melting together 240 grains pure silver, 24 grains pure gold, and 17½ grains pure tin (Professor Wildman). The metals are melted, and the silver is dissolved out as described in No. 3, by adding nitric acid to the alloy,

when a strong chemical action is set up.

The acid reduces the alloy to a fine state of division, and is added until all action ceases. The acid is now poured off, the filtrate washed repeatedly with water, and the tests for silver made by adding common salt. If no white precipitate forms, the powder is washed in absolute alcohol and bottled.

Purple of Cassius shows great variations in colour even when made from the same formula. Its colour can frequently be improved by treating it with nitric acid immediațely before using.

Casting of Gold.—The metal is cast in carats, ranging from pure gold to carats as low as 15 for dental work. The casting machines may be of the centrifugal type, steam or air pressure, or the vacuum casting machine such as the Elgin. For inlay work, pure gold, platinized gold, and crown gold of 22 carats, are employed, each having its special application. Pure gold in the front of the mouth in exposed positions where the inlay is not carried to the incisive edge. Pure gold with a trace of platinum for biting surfaces and edges, the platinum increasing the hardness and strength of the metal when exposed to attrition. Crown gold formulæ where greater strength than pure gold affords is necessary, and where a platinized gold is not acceptable to the operator.

For cast crown tops and porcelain crown bases, crown gold gives good results. For denture bases 20 and 18 carats are employed; also 17 carat platinized gold where the elastic property and increased strength imparted by platinum is desired. It should always be borne in mind that cast gold does not possess as much strength as the rolled or drawn metal.

Hammering and swaging after casting, accompanied by careful annealing, modifies the tendency of the cast metal to fracture; but this is not always possible, hence the metal is cast slightly thicker, and weak positions strengthened in addition. Gold is improved in its casting properties if not heated greatly in excess of its melting-point, and cleaned thoroughly before a casting is done. Some of the investing compounds seem to favour the formation of a slag in combination with borax, and pickling only separates the surface slag adhering to the gold from the investment after the cast has been run. On melting the gold on Fletcher's melting tray, sparks frequently are given off, and the gold is disturbed until the sparking ceases. The addition of a slight trace of borax and sal ammoniac quickly separates the impurities, and the gold runs clear into the ingot mould. Castings, and especially imperfect castings, at times are intensely brittle, and on filing glass-like particles are met with. This is traceable to some of this siliceous slag being forced or drawn into the casting with the liquid metal. As little borax as possible should be employed during the melting and casting of the gold—only sufficient to keep the metal clear and bright.

### CHAPTER XI

## PLATINUM

Symbol, Pt. Specific gravity, 21.50.

Atomic weight, 195.0. Melting-point, 1,745° C.

Occurrence.—Platinum occurs principally in the metallic state, and frequently in the same alluvial deposits as gold, as nuggets and flattened grains of various sizes. It is most frequently found associated with the metals iridium, palladium, osmium, rhodium, and ruthenium, these metals with platinum composing the "platinum group " or " platinum metals." Native platinum contains from 60 to 80 per cent. of platinum, the remainder being some of the other metals of the group, with traces of gold, copper, and iron. The metal also occurs combined with silver, gold, copper, and iron, also in the mineral sperrylite (PtAs<sub>3</sub>), which contains 50 per cent. platinum and 40 per cent. arsenic. Native platinum is used as a source of the metal. The chief impurities found in the native metal are quartz, spinel, corundum, titanic, chrome, and magnetic iron ores, gold, osmoiridium, serpentine, and zircon.

**Preparation of Platinum.**—In the extraction of platinum the ore is concentrated by washing, and any gold in the free state removed by mercury, which amalgamates with this metal, leaving the platinum free. The processes may be divided into two—the wet and dry methods.

Wet Methods—(I) The Wollaston Extraction Process.— This process depends upon dissolving the other metals present with the platinum, and leaving the platinum as a deposit, or bringing the platinum to solution, and leaving such metals as osmium and iridium as the deposit. The platinum ore is digested with nitric acid, which dissolves out the copper, silver, iron, or lead, present. The residue is washed to free it of any nitrates, and then digested with hydrochloric acid, and heated to dissolve out any magnetic iron present. Again it is washed, more hydrochloric acid added, and heated, and small quantities of nitric acid added from time to time. Platinum chloride is formed, leaving iridium, palladium, and osmium, as a residue. The platinum chloride solution is mixed with ammonium chloride, which deposits the platinum as ammonia chloride of platinum. The double chloride is heated in plumbago crucibles to drive off the ammonia, and the platinum is left as a grey spongy mass, known as "spongy platinum," which is annealed to redness and rolled, hammered, or pressed into sheet, etc., or fused by the oxyhydrogen flame, and run into ingots. This process is best adapted for extracting platinum in which the gold is present in very small traces; it fails, however, to remove the iridium and rhodium present.

(2) Schneider's Process.—To remove iridium and rhodium: The solution of platinum, after the palladium, osmium, and part of the iridium, have been removed, is evaporated almost to dryness; it is then diluted with water, soda added until the solution is alkaline, and the mixture boiled with alcohol. The precipitate from this is dissolved in hydrochloric acid, and ammonium chloride added, when the platinum is deposited as the pure double chloride.\* The iridium and rhodium are converted to the sesquichlorides, which are not precipitated by the addition of ammonium chloride. The wet method is principally used for the extraction of platinum.

<sup>\*</sup> Schnabel and Louis, vol. ii., p. 783: "Schneider's Process."

Dry Methods—Deville and Debray Process.—In this dry process the intention is to concentrate the gold, platinum, iridium, osmium, etc., in lead, and cupel the alloy thus formed, afterwards separating the metals by one of the parting processes, as given under Gold. When a platinum ore is treated, the iridium, osmium, and palladium, if present, fall to the bottom of the lead, and by concentrating these, by removing the more liquid lead from time to time, these metals are removed and recovered separately as granules. The lead containing the platinum is cupelled, when the metal is recovered as the spongy platinum, which is either rolled, hammered, pressed, or melted, as already described under the Wollaston Process. Another method, a combined wet and dry process, is to alloy the platinum with 6 parts lead, and granulate the alloy by pouring it into water. It is then digested in dilute nitric acid to dissolve any copper, iron, palladium, and part of the rhodium. The filtrate is digested in aqua regia, which dissolves the platinum, lead, iridium, and osmium. The lead is then deposited by sulphuric acid, and the platinum by adding chloride of ammonia and sodium. The chloride of platinum thus formed is melted with potassium and ammonia bisulphate, and any rhodium present washed out with water. The platinum is recovered as the spongy platinum.

The Deville Furnace.—This furnace, for use with the oxyhydrogen flame, is made of two blocks of calcined lime hollowed in the centre, and clamped together with iron bands. The nozzle of the blowpipe is platinum-tipped, and let into the furnace from above, the aperture also being lined with platinum. Coal gas is conveyed through one tube, the oxygen passing through another and meeting the coal gas at the point of ignition. The products of the combustion pass through a tap-hole let into one end of the lime block, and through which also the melted platinum is poured. A fresh furnace is

required for each melting.

Electro-Deposition of Platinum.—The electrolyte is an acid solution of gold chloride with excess of hydrochloric acid. The anodes are sheets of gold, alloyed with the metals of platinum group, silver, copper, etc.; the cathodes are of pure gold-foil. The tensions are low, and the gold from the anode only is deposited; the platinum, being alloyed with the gold, passes into solution, enriching the electrolyte, but is not deposited. The other metals are not dissolved, but collect at the anode as a slime. This process is not much in favour, as the other processes are quite efficient.

Properties of Platinum.—In colour platinum is a dull grey unless when rolled, when it is bright and of a white colour. When pure it is very malleable, ductile, and very tenacious. It does not oxidize at ordinary temperatures. The solvents for the metal are aqua regia and potassium cyanide in concentrated solutions. Nitric, sulphuric, and hydrochloric acids have no action upon the metal. In the mouth platinum is not affected by oral secretions, a property of great value in the making of pins for artificial teeth, especially for vulcanite work, where, through the contraction of all forms of vulcanite, the pins, if made of base metals, are liable to oxidize. Its high melting-point, 1,745° C., is especially valuable in bridge work, continuous gum work, and as a matrix metal where high fusing porcelains are used for inlays. It is employed for wiring electric furnaces, and for trays for firing inlays, continuous gum work, etc. For root canal fillers, needles and points of hypodermic syringes, the property of the metal in withstanding the action of iodine, sulphuric acid, etc., is valuable, where these and other remedies act as corrosives to steel. Platinum possesses the property of occluding gases to a certain extent, and also the remarkable property of inducing chemical combination between oxygen and hydrogen. the combination of these being accompanied by heat. Both these properties are most marked in the variety known as "platinum black," a preparation capable of occluding 800 times its volume of oxygen. It is prepared by warming platinum chloride in caustic potash dissolved in alcohol. Like silver, the metal absorbs oxygen when molten, giving it up again when cooling, and "spitting" as in the case of silver. It ranks amongst the heaviest of the metals, as is seen from its specific gravity. The metal is extremely ductile, and Essig instances the wire drawn by Wollaston: by plating with silver and passing through a draw-plate and then dissolving, the silver produced a wire  $\frac{30000}{1000}$  inch in diameter, I grain of which would, if extended, stretch one mile. Platinum is seldom found pure in commerce, as the following analyses show:\*

- (1) Platinum, 99.9; rhodium, 0.01; arsenic, 0.01.
- (2) Platinum, 99.9; iron, 0.0001.
   (3) Platinum, 99.29; iridium, 0.32; ruthenium, 0.04; iron, 0.06; copper, 0.07.

Impurities exert a powerful effect upon the properties of the metal, reducing the ductility, malleability tenacity, and generally lowering it in value for dental purposes, except where special effects are sought. Minute traces of iron, zinc, arsenic and carbon render the metal friable and brittle—an effect of much importance in the composition of pins for porcelain teeth. The metal should be annealed at a bright heat for a few seconds and allowed to cool slowly. For the effects of other metals, see Alloys of Platinum.

## Alloys of Platinum.

Platinum and Gold.—The alloy in sheet form is used for bands and base-plates, as foil and matts for filling purposes, the platinum increasing the strength and elasticity of gold generally. The metals alloy readily, the alloy possessing a lower fusing-point than platinum. Platinized gold for clasps and base-plates may contain:

<sup>\*</sup> Comptes Rendus, cxlviii. 1177-1179, May 3, 1909.

Pure gold, 20 dwts.; copper, 2 dwts.; platinum, 1 dwt. (See Gold.) An alloy of 9.5 of gold to I of platinum possesses the same density as platinum, and is infusible in ordinary furnaces. As platinum is increased in these alloys, the tendency is for nitric acid to attack them. In foil form the alloy of gold and platinum is supplied in several shades of colour for filling purposes. It can be obtained so light as almost to resemble a freshlyinserted silver-tin amalgam. The alloy is harder to work than pure gold, possesses greater edge strength in the finished filling, but the colour, especially when given a high polish, is almost black seen in certain lights. In matt form it is generally too red in colour when finished, and, unless the annealing receives very careful attention, the tendency is for the alloy to scale. In foil form the alloy is of service for matrices for fused inlays, the higher melting-point and greater elasticity being valuable properties for this purpose.

Platinum Solder.—Gold 75 parts, platinum 25 parts, yields a solder suitable for using with platinum as a base, or where iridio-platinum is used as sheet, bar, or wire. It is chiefly of use in soldering attachments where high fusing porcelains are used, as in continuous gum work.

Platinum and Iridium.—Iridium added to platinum increases its hardness, elasticity, and raises the fusing-point. For continuous gum work the alloy iridio-platinum contains 10 to 15 per cent. iridium, giving an alloy of great strength, infusible with the ordinary blow-pipe, and mostly used as a strengthening bar for lower dentures, crown posts, etc. The alloy is also used in the making of standard weights, and in traces in certain makes of pins for artificial teeth. Excess of iridium tends to brittleness, while 78.7 parts platinum to 21.3 parts iridium withstands the action of aqua regia.

Platinum and Osmium.—A new alloy, osmiumplatinum, is the subject of a United States patent. The rarer metals of the platinum group are not easily obtained in a state of purity, and therefore no great success has attended efforts to combine them as bivalent alloys. It is now stated that highly refined platinum and osmium have successfully been combined in widely varying proportions yielding alloys of commercial value. Alloys containing I to IO per cent. of osmium and 90 to 99 per cent. of platinum are chiefly used. Great purity of the respective metals is essential to success, as even small percentages of other elements are very detrimental to the properties of the resulting alloy. One part of osmium in an alloy with platinum will take the place of two and a half times its weight of iridium, and this is one of the metals hitherto most used. The new alloy is very resistant to acids, and also possesses great hardness and tensile strength. Wires of the finest calibre are drawn with comparative ease.\*

Platinum and Silver.—The metals alloy well, platinum even in small quantities increasing the hardness, and

lessening the oxidation, of silver in the mouth.

Dental alloy contains from 3 to 15 grains of platinum per pennyweight of silver. Silver in excess of 10 per cent. (the "content") added to platinum causes the alloy to be attacked by nitric acid. Dental alloy may be soldered with 16 and 18 carat gold solders. (See Silver.)

MELTING-POINTS OF DENTAL ALLOY (C. ASH AND SONS).

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No. 1 Dental Alloy .. .. 2,150° F.
No. 2 Dental Alloy .. .. 1,750° to 1,800° F.
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Platinum and Copper.—The metals alloy readily, the resulting alloy resembling gold in colour. Copper lowers the fusing-point of the metal, and is generally added in small quantities to the alloys of gold and platinum. The alloy tarnishes rapidly in the mouth and in air.

Platinum and Mercury.—Platinum and mercury do not alloy well, the platinum requiring an excess of mercury to render the alloy plastic. In dental amalgams,

<sup>\*</sup> Chemical Engineering, xviii., No. 3, through Chemical News, August 7, 1914.

platinum has been displaced to a large extent on account of this property, its place having been taken by zinc. (See Amalgams.) Platinum alloyed with tin, lead, and zinc, yields alloys brittle and friable, and of little practical utility.

## IRIDIUM

Symbol, Ir. Specific gravity, 22.42. Atomic weight, 193·10. Melting-point, 2,500° C.

**Occurrence.**—Iridium occurs chiefly associated with platinum, and in the alloys iridosmine and osmoiridium associated with osmium. It also occurs in several golds, especially in gold obtained from California and British Columbia.

**Preparation.**—The alloy of iridium and osmium is generally found as very fine granules, is intensely hard, and insoluble in aqua regia. To extract the iridium, the alloy is fused with five times its weight of zinc, the zinc volatilized, and the alloy osmoiridium crushed and sifted. The sifted alloy is mixed with barium peroxide, kept at a white heat for an hour, and boiled in aqua regia. The osmium is thus converted into osmium peroxide (OsO<sub>4</sub>), which, when heated to 100° C., passes off as a pungent and poisonous vapour. The iridium remaining in solution is separated as the insoluble double chloride by the addition of potassium chloride, the barium having been removed previously by adding sulphuric acid. The iridium is recovered from the double chloride.

**Properties.**—Iridium is a steel-white metal possessing great strength, brittle when cold, but moderately malleable if raised to a red heat. It is seldom used separately, the alloy iridio-platinum being its usual form in use. (See Platinum.)

The alloy osmoiridium as the fine granules, found native, is largely made use of for pointing fountain-pens

being hard, insoluble in aqua regia, not oxidizing in the presence of moisture or air. A compound of iridium with 7 per cent. phosphorus is also largely used for this purpose.\* Iridium generally contains traces of platinum and ruthenium, is not acted upon by the acids when pure, but if oxidized at a red heat in hydrogen is dissolved in aqua regia. Apart from the alloys already given, the metal has no general application.

## **PALLADIUM**

Symbol, Pd. Atomic weight, 106·70. Specific gravity, 11·50. Melting-point, 1,535° C.

**Occurrence.**—Palladium is found in the ores of platinum in quantities seldom exceeding I per cent. It also occurs occasionally in the native state, comparatively pure, associated with platinum.

**Preparation.**—The metal is obtained chiefly by the parting process from the solution of the crude double chloride of platinum, after the platinum has been procipitated. Sodium carbonate and a solution of cyanide of mercury is added. Palladium cyanide is formed, which, when heated, and the mercury driven off, yields metallic palladium.

Properties.—Palladium is the most easily fused of the platinum group, the melting-point being almost equal to that of wrought iron. It is readily dissolved in hot nitric acid. In colour the metal is white, with a slight tinge of yellow, resembling an alloy of platinum and gold with excess of platinum. The metal is malleable, fairly ductile, harder than platinum, and is oxidized slightly if heated to redness in air. The solvent for palladium is aqua regia. It is attacked by iodine, and may thus be distinguished from platinum, on which iodine has no effect. As a constituent of dental amal-

<sup>\*</sup> Huntingdon and Macmillan, p. 524.

gams, the metal at present has fallen into disuse. Its scarcity, cost, and the fact that the amalgams formed showed excessive expansion, led to its abandonment. The addition of mercury is accompanied by heat, even when palladium is alloyed with other metals. The amalgams also discolour to a great extent, the blackening tending to permeate the tooth structure. The metal occludes 643 times its volume of hydrogen if heated to redness, the absorption of the gas being accompanied by an elevation of temperature.

Alloys of Palladium.—The metal alloys readily with most other metals, but its comparative scarcity and cost

prohibit its gentral use.

Palladium Alloy.—An alloy of silver and palladium possessing almost similar properties and uses as dental alloy. Is malleable, ductile, and can be readily swaged in sheet form. Possesses a lower atomic weight than dental alloy, I ounce in sheet of similar thickness covering a surface 25 per cent. greater than the platinum alloy.\* The metals alloy well, and disclose little tendency to separate on heating.

<sup>\*</sup> C. Ash's Circular, August, 1910.

## CHAPTER XII

## **TANTALUM**

Symbol, Ta. Specific gravity, 16.6.

Atomic weight, 181.8. Melting-point, 2,770° C.

**Occurrence.**—The metal usually occurs in its ores together with columbium, a metal closely resembling tantalum in its physical properties. It occurs in America, Australia, Scandinavia, and South-West Africa. The Australian ores are called "tantalites," and contain from 50 to 70 per cent. of tantalic anhydride ( $\text{TaO}_5$ ). In American ores, columbites, the oxide varies from 10 to 40 per cent. The metal occurs chiefly as iron and manganese tantalites.

**Preparation.** — Tantalum belongs to the vanadium group of metals, and is obtained from tantalic acid obtained from the ores. This is first converted by suitable chemical treatment into a white double salt, the fluoride of potassium and tantalum (K<sub>2</sub>FeTaF<sub>5</sub>). By the reduction of this double salt, pure tantalum is obtained in the form of a greyish-black metallic powder, which, on being melted at very high temperatures in an electric vacuum furnace, yields a lustrous grey regulus.\*

**Properties.**—Pure tantalum closely resembles platinum in colour. It is ductile, malleable, and possesses great toughness, with a tensive strength equal to 58 tons per square inch. In hardness the metal equals mild steel; the pressure of even small quantities of the oxide of the

<sup>\*</sup> Siemens and Halske.

metal increases the hardness considerably. The metal is non-magnetic, is not affected by exposure to air at ordinary temperatures; is not attacked at any temperature by alkalies or single acids, with the exception of hydrofluoric acid. When heated beyond 600° C., the metal becomes covered with a layer of white tantalum oxide, and gradually burns. Tantalum chloride is formed by acting on the metal with chlorine, which volatilizes and condenses to yellow crystalline masses on cooling. Copper, silver, platinum, nickel, and zinc, can be deposited from solution, using a cathode of pure tantalum. The metals deposit on the cathode, from which they can be removed by acids or aqua regia without affecting the tantalum. The anode may either be of platinum or of platinum-covered tantalum.

Dental Uses.—The resistance of tantalum to chemicals. its great hardness, elasticity, and the readiness with which it can be rolled, hammered, drawn, turned, and shaped into any desired form, have led to its use for dental and surgical instruments. Such instruments do not rust when immersed in sterilizing solution or on being boiled in acids, and are not affected if heated in a naked flame up to a dull redness. Beyond this temperature the metal oxidizes. They are not affected by iodine, sul-phuric acid, or any of the other remedies employed in the mouth by the dental profession; and for nerve canal fillers, probes, hypodermic needles, etc., has displaced platinum to a considerable extent. At present, scalers, spatulas, burnishers, nerve broaches, root canal drills, dividing files, discs, expansion arches, etc., are in use, and have proved satisfactory. Edge tools prepared from the metal can be ground and sharpened like steel, and do not require to be tempered.

### CHAPTER XIII

## ALUMINIUM

Symbol, Al. Specific gravity, 2.56.

Atomic weight, 27·10. Melting-point, 657° C.

## Occurrence.

Bauxite, (Al<sub>2</sub>Fe)O<sub>5</sub>H<sub>4</sub>. The hydrated oxide associated with iron.

Corundum, Al<sub>2</sub>O<sub>3</sub>. The oxide well known as an abrasive agent.

Diaspore, Al<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O. A hydrated oxide.

Cryolite, Al<sub>2</sub>F<sub>6</sub>6NaF. Double fluoride of sodium and aluminium.

Cyanite, Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>.

Bauxite is the chief source from which aluminium is procured; it contains about one-third aluminium, together with oxide of iron, silica, oxygen, and water.

Cryolite is found in abundance in Greenland, and contains 13 per cent. of the mineral. Aluminium is never found in Nature in the metallic state, but is present in all varieties of clay (silicates of aluminium), varying in amount from 10 to 20 per cent. It also occurs in such precious stones as—

Ruby and sapphire,  $Al_2O_3$ ; cyanite,  $Al_2O_3SiO_2$ ; topaz,  $Al_2SiO_4Fe_2$ ; garnet,  $(CaMgFeMn)_3Al_2Si_3O_{12}$ ;

kaolin or china clay, Al<sub>2</sub>O<sub>3</sub>2SiO<sub>2</sub>.2H<sub>2</sub>O.

Preparation of Aluminium.—Wholer, in 1828, was the first to obtain aluminium by the decomposition of aluminium chloride, using potassium; and it was the practice to effect the reduction by means of sodium or

potassium, sodium being preferred owing to the action set up being less violent, and the cost less. The atomic weight of sodium being lower also favoured the decom-

position of a greater weight of aluminium.

Modern Electro - Smelting Process. — The cryolite, fluorspar, or other mineral, is reduced to a rough powder, which is packed in large boxes or furnaces around the carbon rods; these (negative and positive) are connected with a powerful dynamo. The great heat reduces the metal, which sinks and is tapped off from the bottom. Fresh ore is added, and the process is not interrupted. There are many modifications of this process, but the differences are in details. In the Hall process, for instance, the carbons are generally about forty in number, each about 3 inches in diameter and 18 inches long (Essig). As long as the carbons are in contact with the furnace charge, the resistance offered by the charge is very low; but when the aluminium is reduced, the resistance increases, which increase lights an incandescent lamp, and signals that the furnace requires recharging. The process may thus be continuous.

Cowles Process.—The Cowles process depends upon the great heat generated by the electric arc for the reduction of the metal. A mixture of 2 parts powdered corundum and charcoal and 2 parts granulated copper or copper oxide is packed into rectangular vessels. Into the powder are led carbon rods, and the poles connected with a powerful dynamo. As the great heat generated melts the charge, the carbon rods are gradually withdrawn. The presence of copper facilitates the reduction of the aluminium, an aluminium bronze being formed.

**Properties of Aluminium.**—In colour the metal is white, tinged with blue, and is capable of receiving a very high polish. Aluminium by some writers is given a position between the noble and base metals; by others it is regarded as base. It is very malleable and ductile, and these properties are considerably increased by careful annealing. Rolling increases the specific gravity

from 2.60 to 2.70. Aluminium is among the lightest of the metals, and is employed for small weights. For conductivity of heat and electricity it almost equals silver. It does not oxidize in the air or sulphuretted hydrogen, and is highly sonorous, this property being influenced by the shape of the casting. Faraday points out that there are two tones present—a longitudinal and a transverse—instead of a single tone, with its corresponding upper tones, as in a bell of silver. Aluminium, being a highly electro-positive element, is capable of reducing a number of metals from combinations with oxygen and sulphur. Thus, when finely divided and heated with the oxide of manganese, chromium, tungsten, or uranium, along with lime to form a slag, an energetic action takes place: the aluminium combines with the oxygen, and the metals are obtained as a coherent mass (Newth). The Thermil process of welding depends upon the strong exothermic reaction between aluminium and oxide of iron. Boiling nitric acid acts on the metal slowly. Dilute nitric, sulphuric, acetic, and tartaric acids have no sensible action upon it. Hydrochloric acid is the best solvent, evolving hydrogen. Hydrates of sodium and potassium in solution readily attack the metal, evolving hydrogen. The fact that iodine has no action upon aluminium has led to its use for dressing forceps, canal fillers, etc., in applying this antiseptic. Aluminium, when cast, shows contraction on cooling. It is best cut with single-cut files.

**Dental Uses.**—Aluminium has been used to a certain extent as a metal for base-plates, cast dentures, impression trays; as a constituent of aluminium bronze; and for many purposes where lightness, strength, and freedom from oxidation, are essential, such as mouthprops, sections of face-pieces, etc. Its white colour, lightness, freedom from oxidation in the air or moisture, its strength, malleability, and ductility, combined with its cheapness, have encouraged the profession in its application. For base-plates, either to be struck or

cast, the purer the aluminium the better it withstands the solvent action of saliva, and the more malleable it becomes, its properties generally being markedly improved.

Care should be taken to avoid contact between aluminium and the zinc and lead used as die and counterdie, as these metals exert a deleterious effect on aluminium if present even in small quantities, inducing pitting of the surface, and ultimately, by galvanic action, a gradual solution. A pickling solution of 50 per cent. nitric acid used hot before each annealing cleanses the aluminium, if contact has occurred. So far the efforts made to gild aluminium when employed as a base-plate for dentures, in order to protect the metal from the solvent action of alkaline salivas, has not been accompanied by uniformly good results.

To Frost Aluminium, place the metal in a solution consisting of one stick of caustic soda or potash to 4 ounces of water for three to five minutes, and pickle

in 50 per cent. solution of nitric acid.\*

Soldering of Aluminium.—The rapidity with which aluminium oxidizes at soldering temperatures, and the insoluble nature of the oxide formed, have always rendered the soldering of the metal difficult. Professor Richards holds that the solder should contain its own flux, so that the instant the solder flows the flux will clean the surface, and so make union possible. Silver chloride has also been recommended as a useful flux, the silver being deposited on the surface, and thus preventing oxidation.

The following solders are recommended:

## COMMON SOLDER.

Copper	• • • •	 4 parts.
		 ··. 6 ,,
Zinc		 90 ,,

No borax is used. Adhesion is induced by friction with small tools made of aluminium (Turner).

<sup>\*</sup> Elliot's Quarterly, April, 1910, p. 15.

HARD SOLDER FOR ALUMINIUM.	SOFT SOLDER (FRISMUTH).
Pure block tin 90 to 98 parts. Bismuth 1 to 5 ,, Aluminium 1 to 5 ,,	Pure block tin 90 to 99 parts. Bismuth 10 to 1 part.

Vaseline as a flux for these.

### THOWLES'S SOLDER FOR ALUMINIUM.

Tin					55 part	s.
Zinc	• •				23 ,,	
Silver	• •	• • •	• >•	•••	5 ,,	
Alumini	lum				2 ,,	

The surfaces to be soldered are washed in dilute caustic alkali or cyanide solution, and dried. No flux is used.

The following are useful solders, for soldering tray-handles, etc.:

Zinc	 	 62.50 per cent.
Tin	 	 25.00 ,,
Lead	 	 12.50 ,,

Paraffin wax as a flux.

-SELLONS.

Cadmium	 	 	50 parts	3.
Zinc	 	 	20 ,,	
Tin	 	 • •	30 ,,	

Also a soft solder.

-The Scientific American.

## ALUMINIUM SOLDERS.

Aluminium	20 parts.	Aluminium	8 parts.
Zinc	8o	Zinc	92

Flux consists of 3 parts balsam copaiba, 1 part of Venetian turpentine, and a few drops of lemon-juice. Dip soldering-iron into mixture.

Zinc			 2 ounces.
Tin			 2 ,,
Antimony -			 33 grains.
Salicylic acid	• •	• •	 ΙΙ ,,

The metals are melted together and the acid added, a blowpipe being used during the soldering.

—The Brass World.

So far the soldering of aluminium for dental purposes has not proved satisfactory, and, wherever possible, it is better to reduce soldering to a minimum.

# Alloys of Aluminium.

*Tiersagent*, an alloy containing two-thirds aluminium and one-third silver, used as a cheap substitute for silver, is much harder, and does not readily oxidize.

Aerdentalloy.—An alloy said to contain 90 per cent. aluminium, 5 per cent. silver, and 5 per cent. tin. It is only used in the casting processes, and gives good results when employed for lower base-plates. (See Casting of Aluminium.)

Magnalium.—A proprietary alloy said to contain aluminium with a trace of magnesium. Has a lower specific gravity than aluminium itself, is very bright when cast, and is generally cast for upper base-plates where great lightness is desirable.

Aluminium Gold.—78 48 per cent. gold and 21.52 per

cent. aluminium; may be struck in sheet or cast.

Aluminium Silver.—Copper, 70 parts; nickel, 23 parts; aluminium, 7 parts. An alloy said to receive a high lustre and polish, and to swage well when frequently annealed at a bright red heat.

Aluminium Tin.—100 parts aluminium, 10 parts tin. This alloy is a little heavier and whiter than aluminium.

The alloy can be welded and soldered like brass.

Aluminium combines readily with iron, the metal reducing the melting-point of iron very considerably. Iron also takes on a coating of aluminium in much the same manner as it does with tin.

Casting of Aluminium.—Aluminium is cast either as the pure metal, or alloyed with such metals as silver and tin, magnesium, or tin. Pressure casting or the swinging bucket method seem to answer best. Care should be taken to avoid overheating, and consequent oxidation of the metal, which should be brought to the

liquid state in a separate crucible. The metal has the property of storing heat, and will be observed to become more liquid after the thick pasty state has been reached and the heat withdrawn. Aluminium never runs clear and watery like clean gold, the movement of the metal when poured being slower and more resembling a flop, very much like the movement of impure mercury over a flat surface.

Corundum and Emery.—Corundum is obtained from India, Ceylon, and several parts of America. The mineral, an oxide of aluminium, occurs in large masses and as hexagonal crystals. For grinding-wheels it is ground to powder, mixed with shellac, and pressed into moulds. Next to diamond, corundum is the hardest mineral known. Carborundum, which is still harder, is not a mineral, but is manufactured. (See Carborundum.)

Emery, an impure form of corundum, is also an oxide of aluminium. It is also obtainable in various degrees of coarseness, or in various "grits" like corundum, and is made into wheels in the same manner. It is used in the laboratory, in the powdered state, mixed with oil, for polishing metal dentures, taking a better grip of the surface than pumice, and removing scratches, file-marks, etc., more rapidly. Gummed on cloth strips, it is useful for polishing gold and amalgam fillings, and for polishing-wheel marks on artificial teeth, before putty powder is used.

Carborundum.—Carborundum, a carbide of silicon, is manufactured from coke, sand, a small quantity of common salt, and sawdust. The furnace is charged with these packed around a central core of coarse coke, and an electric current of high voltage is passed through the mixture, which results in carborundum. Near the centre of the charge the carborundum is in large irregular crystalline masses, graduating towards the sides into an amorphous powder. The various-sized crystals are separated by sifting, the larger ones,

broken up, mixed with a vitreous silicate, and fired in a crucible furnace until the binding agent has fused. In the small stump and cavity stones the binding material more closely resembles shellac, as the stones wear in much the same manner as corundum if not kept moist with water or lubricated with vaseline to reduce friction heating. Carborundum is much harder and cuts faster than corundum or emery, having displaced these to a great extent in the dental laboratories, etc. Dilute nitric acid is used to free carborundum stones and wheels from accumulated grit.

### CHAPTER XIV

## NICKEL

Symbol, Ni. Specific gravity, 8.80.

Atomic weight, 56.68. Melting-point, 1,427° C.

**Occurrence.**—Nickel occurs chiefly combined with arsenic, and was first mentioned by Hiarni in 1694 under the name of "leupfernickel," signifying "false copper," from the fact that it resembled copper ore, and still did not yield copper. Cobalt is almost invariably combined with the metal in the ore.

The chief ores are—

Garnierite, NiMg(SiO<sub>3</sub>)<sub>2</sub>3HO. A hydrated silicate of the metal containing from 7 to 10 per cent. nickel. It is usually associated with oxides of iron and siliceous gangue.

Nickel-blende, NiS.

Antimonial nickel, NiSb.

White nickel, NiAs,.

Millerite, or nickel pyrites, NiS. A yellow-coloured sulphide.

Nickeliferous pyrites, or pyrrholite, the magnetic

pyrites, 10 to 15 per cent. nickel.

Kupfernickel, or niccolite, Ni<sub>2</sub>As<sub>2</sub>, an arsenide of nickel.

**Preparation of Nickel.**—The processes for the reduction of nickel ores depend on what metals occur combined with nickel. They may be divided into two classes—the dry and wet processes.

Dry Processes.—The dry processes for the reduction of nickel are extremely varied, the variations depending to a great extent upon what impurities, or what other metals, are combined with the ore. The presence of cobalt causes the processes generally to be much lengthened. The one given may be regarded as showing the essential operations. When an ore of nickel containing sulphur is being reduced, 7 per cent. sulphur is left in the ore after the first roasting. The ore is then mixed with coke or charcoal and calcium sulphide, and heated in a blast-furnace, when the slag combines with the silica and other materials in the ore, and is run off. The matt so formed is treated in a modification of the Bessemer converter, when most of the sulphur and all the iron present are eliminated in the slag. The matt is ground to powder, mixed with sulphate of soda and coal, and remelted in a cupola. Any copper present separates on cooling; the two metals and the two matts are then remelted separately until the copper is free of nickel, and the nickel free of copper. The remaining sulphur is driven off, leaving the nickel present as the oxide, which is mixed with flour and oil into a paste, heated to a white heat with charcoal, when metallic nickel results, but is unfused. This "grain" or "cube" nickel is placed in iron pots, and heated in a reverberatory furnace until the nickel is compact and coherent.

The Mond Carbonyl Process.—This process consists in passing pure carbon monoxide over gently heated metallic nickel at 60° C.,\* when a curious volatile compound known as nickel-tetra-carbonyl, Ni(CO)<sub>4</sub>, is formed. This liquid boils at 43° C., forming a vapour which, if heated to 180° C. and led into chambers containing granular nickel, splits up into carbon monoxide and nickel. The CO<sub>2</sub> having no action upon copper or cobalt, and but little action upon iron, the nickel is thus obtained almost pure, deposited upon the grain

nickel.

<sup>\*</sup> Schnabel and Louis, vol. ii., p. 636.

Wet Processes.—I. The ores are washed, picked, and roasted to drive off volatile compounds, such as arsenic, sulphur, etc. They are then digested with boiling hydrochloric acid; bleaching powder is added to peroxidize any iron present, which is precipitated as the oxide and basic arsenide of iron. Sulphuretted hydrogen is passed through the solution, and deposits any copper present as the sulphide. The solution is next boiled to drive off any sulphuretted hydrogen, and neutralized with lime. Any cobalt present is deposited by adding a little bleaching powder, and the solution filtered. Milk of lime is now added, and the nickel deposited as the hydrated oxide.

2. Nickel may be obtained as a black powder by reducing nickelous oxide in a stream of hydrogen, or by reducing nickelous oxalate out of contact with air.

3. The metal can also be obtained by the electrolysis of an ammoniacal solution of the double sulphate of nickel and ammonia.\*

**Properties of Nickel.**—Nickel is grey in colour, almost approaching to whiteness. It is ductile, malleable, weldable, and of great tenacity and hardness, almost equalling iron. These properties, combined with its high melting-point and its freedom from oxidation in water, have led to its use, when alloyed with other metals, as a cheap substitute for platinum for pins in artificial teeth, posts for crowns, plate of backings, bridges, etc. (See Alloys.)

In the pure state it is used as a substitute for platinum for muffles of dental furnaces, firing trays, and as a constituent of cheap dental amalgams. Nickel spatulas are better for use in mixing cements for filling purposes, as some of the finer tints are darkened if unplated steel is used for the purpose. As contained in nickel silver, it is used for impression trays, and in many appliances where a white metal is of advantage. Cobalt is nearly always present in commercial grades of nickel, the

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separation of these metals being very difficult and expensive. Commercial nickel rarely contains less than from 56 to 86 per cent. of nickel, and an analysis by Lassaigne gives a return as follows: Nickel, 73.30; cobalt, 22.10; iron, 1.0; alumina, 2.50; and silica, 0.50, plus a trace of copper (Greenwood). The metal does not readily tarnish or oxidize in air, but finely powdered, as obtained by reducing the oxide in a current of hydrogen, it is spontaneously inflammable; and heated and immersed in oxygen it burns like iron. Nickel is magnetic at ordinary temperatures, but loses this property if heated to 250°C. It is not acted on by water, and is used as a protective coating for articles made of steel or iron, such as surgical instruments, appliances, etc., by a process of plating. Added to steel it forms an alloy, nickel steel, having a high elastic limit and offering great resistance to penetration. (See Steel Alloys.) Nickel is soluble in nitric acid, and dissolves slowly in dilute sulphuric and hydrochloric acids.

Alloys of Nickel.—The chief use of nickel in industry and the arts is in its application in a valuable series of alloys, and for plating.

**Nickel Silver.**—Copper, 5 parts; nickel, 2 to 3 parts; zinc, 3.5 parts. As in plate it contains—Copper, 5 parts; nickel, 2 parts; zinc, 3 parts.

Preparing Nickel Silver.—To make nickel silver, fuse equal parts of nickel and copper together in crucibles; then add balance of copper, or copper and zinc together as brass.

**Properties of Nickel Silver.**—Nickel or German silver is of a silver-white colour tinged with yellow, the colour differing with its composition. It is chiefly used as a substitute for silver, and as a base for electro-plated ware. For dental purposes it has a wide range of utility, as already noted, possessing great tenacity, ductility, and malleability. In wire form it is useful, when plated, for arch wires in treating cases of malocclusion;

also in sheet form for crowns for raising bites, etc., and for fine instruments which would be attacked by acids if made of steel, such as nerve canal fillers, etc. Its electrical conductivity is low, and is not greatly affected by considerable changes in temperature. The alloy oxidizes rapidly in the mouth; it is usually gold-plated to protect the surfaces of the teeth from contact with the metal, and is only used for temporary purposes. It may be soldered with 18-carat gold solder, although silver solder is usually employed. It should be annealed at a dull red heat for a few seconds at intervals to retain its highest degree of malleability and ductility.

**Platinoid.**—This alloy is used for much the same purposes as nickel silver, but possesses, if anything, greater rigidity than nickel silver. The presence of iron, however, limits its use, as it oxidizes readily when exposed to moisture. It does not solder so readily through oxidation of the surface (probably through the presence of tungsten or iron).

Platinoid contains—

```
Copper ...
                                     60 parts,
Nickel ...
                                     14 ,,
                        . .
Zinc
                                     24 "
Tungsten
                                     -Hiorns.
                                 .. 60.50 per cent.
Copper ..
Nickel
                                     15.97
                . .
                         . .
                                 . .
Zinc
                                     23.00
Lead ..
                                      0.13
                                      0.35
Cadmium
                                      0.13
Loss
                                      0.04
                         -Ash's Quarterly, June, 1907.
```

There are numerous alloys prepared containing copper, nickel, zinc, iron, lead, and tin, the name changing as a rule with the variations in the several metals. Thus we have nickel bronze containing—

```
Copper .. .. 60 per cent.
Nickel .. .. 20
Zinc .. .. .. 12
Tin .. .. 8
```

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This alloy is white and extremely strong, but of no practical application so far in dentistry.

Hall's Metal, a proprietary alloy containing nickel, copper, zinc, and another element,\* is greyish-white in colour and closely resembles dental alloy in appearance and its physical properties. It can be rolled thin enough for pivot crown bases, and can be employed as crown posts, strengtheners for dentures, expansion arches, bands and crowns, for treating cases of malocclusion. The alloy solders with 15-carat gold solders, and can be gilded.

Nickel Steel.—See Steel.

Nickel-Plating.—The solution consists of the double sulphate of nickel and ammonia dissolved in water. Ammonia is added until the solution is alkaline to blue litmus-paper. The positive pole is a sheet of pure nickel, and the article to be plated is attached to the negative pole. The plating takes any time from thirty minutes to a few hours, with an electro-motive force not exceeding 5 volts. The solution used in nickel-plating is most unstable, the nickel showing a constant tendency to crystallize out. Water must be added to retain the strength of the solution. The process is carried out in warm solutions. Steel articles are best previously plated with copper; the coating then adheres better, and there is less scaling through oxidation.

<sup>\*</sup> Messrs. R. Buckland and Sons, Ltd., London.

#### CHAPTER XV

### LEAD

Symbol, Pb. Specific gravity, 11.37.

Atomic weight, 207·10. Melting-point, 327° C.

**Occurrence.**—Galena (PbS), the natural sulphide, is the chief source of the metal.

White lead ore, or cerusite (PbCO<sub>3</sub>), the carbonate,

is also an important source of the metal.

Anglesite (PbSO<sub>4</sub>), lanarkite (PbSO<sub>4</sub>.PbO), matlockite (PbCl<sub>2</sub>PbO), pyromorphite (3Pb<sub>3</sub>.P<sub>2</sub>O<sub>8</sub>PbCl<sub>2</sub>), are other sources.

The natural sulphide and carbonate are the most abundant sources of the metal for commercial purposes. Galena generally contains traces of silver, and is treated specially for the extraction of silver, even when the silver is as low as 2 parts per 1,000 of lead. The ore generally contains about 87 per cent. lead and 13 per cent. sulphur. Antimony is the chief impurity present as the sulphide of the metal. The carbonate, less abundant than the sulphide, is generally reduced with galena, and usually contains close on 78 per cent. of lead; it also contains traces of silver, chiefly as the chloride, iodide, and native silver.

**Preparation of Lead.**—There are three main processes: I. The Air Reduction Process.—In this the galena is roasted to such an extent that part of the sulphide is changed to the oxide and sulphate, so that there are present definite proportions of each. The temperature is increased, and the sulphate and oxide react upon the

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unchanged sulphide; metallic lead is reduced, and sul-

phur dioxide given off.

2. Roasting and Carbon Reduction Process.—The galena is roasted until it is almost entirely decomposed or converted to lead oxide, with a trace of lead sulphate. It is then reduced by heating with carbon; or the sulphate is converted to lead silicate by melting it with silica after the roasting process is completed, the silicate being then reduced to the metallic state by scrap iron.

3. Iron Reduction Process.—The galena is melted with scrap iron; the iron combines with the sulphur, lead is set free, and a compound of the sulphide of iron and

lead is produced.

The American Air-Cooled Hearth and the Scotch Ore Hearth processes consist in melting the lead in a rectangular cavity, the bottom and sides of which are of cast iron. The front is generally composed of bone ash and crushed galena, this mixture being impervious to metallic lead, and is sloped to carry off the molten lead. Over the hearth are hoods to carry off the lead fumes. The ore is melted, and a blast of cooled air is passed over the molten lead, which is drawn off into iron pots. The blast carries off certain proportions of lead and lead sulphate, the term "lead fumes" being applied to these, which are condensed by passing through long flues or wide chimneys kept cool with circulating water. The escaping lead is deposited as a dust, and is collected and reduced.

In the blast-furnace process the essential features are similar. Against the ore hearth processes, it is held that the workmen are more exposed to the poisonous fumes than in the other processes, and that there is a greater loss of lead through volatilization. The cooler the blast of air, the less is the loss through this cause. The lead from all these processes has generally to be "softened," which consists in remelting to oxidize such metals as antimony, copper, zinc, etc., which rise to the surface, and are removed as a floating scum. The

silver is removed by a special series of processes. (See Desilverizing of Lead.)

Desilverizing of Lead.—There are three main processes: I. Pattison Process.—This process is based upon the fact that if there are present 800 ounces of silver to the ton of lead, the two metals form a eutectic alloy. and, on cooling from the molten state, show no tendency to separate or liquate. When silver is more or less present, however, the two metals disclose a constant tendency to separate. Advantage is taken of this property, the silver being seldom in excess of 500 ounces to the ton of lead. The argentiferous lead is melted, and cold water sprayed over it, which causes the crystals of pure lead to form on the surface. These are then ladled out and remelted in a second pot. The process is continued through five or six pots, until pure lead is obtained at one end of the series, and the concentrated silver and lead alloy at the other. The silver is recovered by cupellation. (See Gold.)

2. Luce-Rozan Process.—This is considered to be an advance on the Pattison process, hand labour being done away with in the stirring, cooling, and ladling of the lead. The apparatus consists of two pots, one at a higher level than the other. The lead is melted in the higher, and jets of water and steam are played upon it, to hasten the crystallizing of the lead. This cooling is continued until two-thirds of the charge has crystallized, and the remaining liquid third is then drained off through pipes controlled by valves, the crystals being retained, by means of perforated plates, into the lower pot. In this process subsequent softening of the lead is unnecessary, as the steam, the stirring, and the disturbance of the molten metal, cause such impurities as are present to rise to the surface as a scum, when they

are ladled off.

3. Parkes Process.—This process depends upon the recognized tendency of gold and silver to alloy with zinc in preference to lead, if both metals are present

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in the alloy, and also on the fact that lead and zinc, if alloyed, tend to separate on cooling. Zinc is added to the lead to the extent of  $\mathbf{1}\frac{1}{2}$  per cent. for every 50 ounces of silver present per ton, the whole charge thoroughly melted, stirred, and allowed to cool. The silver combines with the zinc and crystallizes on the surface, and is ladled off into another pot, where the process is repeated. The zinc, highly charged with silver, is finally transferred to a retort, with a little charcoal, and distilled, when the zinc is volatilized and afterwards condensed, leaving the silver in the retort.

Properties of Lead. — Lead is a bluish-grey metal, possessing a bright metallic lustre when freshly cut; this lustre becomes quickly dimmed by the superficial oxidation of the metal in contact with air. It ranks amongst the softest of the metals, and can be readily cut into slices, to which property the term "sectile" is applied. It is readily marked by swaging, and quickly receives impressions. It is malleable and ductile, but its tenacity is very low, and it can only be drawn into thin wire with difficulty. The metal can be welded, and applied to paper leaves a grey mark. When struck, it emits the proverbial dull sound, but is slightly sonorous if cast in mushroom shape and struck. Lead may be readily deposited from a solution of the acetate by zinc or electricity. Its conductivity is very low; it has no taste, but possesses a peculiar odour when freshly cut. Commercial lead, either in ingot or sheet, is fairly pure, the percentage of such metals as silver, iron, tin, antimony, arsenic, etc., being extremely small. Antimony and arsenic harden the metal when present in small quantities, and copper and silver tend to increase the sonorousness.

Lead exhibits a strong affinity for silver, and, besides being found in many ores of silver, the action between the metals is somewhat peculiar. Lead is used in the cupellation process in the parting of gold and silver, advantage in this process being taken of its affinity for oxygen. In his book\* Sir W. Roberts-Austin alludes to this in the introductory historical sketch.

Biringuecio, a contemporary of Paracelsus and Agricola, remarks, "If we had not lead, we should search in vain for precious metals, for without its aid we could not extract gold or silver from stones containing them"; thus showing that it was known that lead was capable of reducing metallic oxides, and liberating the gold and silver from other metals combined with them as impurities. Lead exhibits the property of "flow" to a remarkable extent, even when subjected to pressure in the solid state. Advantage is taken of this in the making of lead piping. The lead is driven under pressure through steel moulds, by this means insuring a homogeneous piping, and one which can be made of indefinite length.

Lead and Oxygen.—The metal combines with oxygen in several proportions, yielding plumbous and plumbic oxides, plumbic peroxide, and combinations of these three. Of these, plumbic oxide, also known as "massicot" or "litharge," is the most important, as it is this compound which, by dissolving metallic oxides, gives lead so prominent a place in metallurgy.

Dental Uses for Lead.—Its most important use is as a counter-die in swaging base-plates; its low melting-point, softness, cheapness, and the numerous meltings it will withstand without alteration of its properties, make it valuable for the purpose. It is also a constituent of lead shot used in swaging, of the soft or tin solders (see Tin), and as centres for polishing-brushes, etc. In swaging gold, using a counter-die of lead, wash-leather or several layers of paper should be used to keep the gold from coming into contact with lead, as the metal has a powerful effect in rendering gold friable and brittle; less than I part lead in 1,000 parts gold makes the gold too brittle to swage.

Lead in the mouth is poisonous, and is not contained

<sup>\* &</sup>quot;Introduction to the Study of Metallurgy."

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in dental amalgams, alloys for bases, etc. Traces of lead are present in some makes of aluminium bronze, the lead facilitating rolling; also in sheet brass and nickel silver. Lead enters into the composition of many of the fusible metals, as Wood's, Roše's, Litchtenberg's, and Newton's. (See Fusible Metals.)

# Alloys of Lead.

Lead and Arsenic: Lead Shot.—Combined with arsenic, which hardens lead, and makes it brittle if in excess, it is used as lead shot for swaging purposes, in making crowns and base-plates. Lead shot is of advantage where Babbit metal or any of the other die metal alloys are employed, as it removes the chances of the die being damaged by having hot metal poured over it.

Lead and Antimony.—In some works antimony is added to lead in the making of lead shot, the metal having a hardening effect on the lead. The metal is also added to lead in type metal. For large type from  $\frac{1}{8}$  to  $\frac{1}{4}$  per cent. of antimony is added; for small type tin is added, and in other forms copper and iron. The alloy of lead, antimony, and tin, or that of lead and tin, is used as counter-die metals, the hardening effect of the antimony and tin helping to overcome any tendency towards change of shape during swaging. In the lead and antimony alloys there is considerable waste through oxidation.

Lead and Tin.—Besides the alloy already given for swaging purposes, lead and tin enter into the composition of soft solders, the proportions of the metals varying according to the purposes for which the solders

are intended.

Examples.—Fine solder contains I part lead to 2 parts tin (as for dental use).

Soft or common solder contains equal parts of lead and

tin (tinsmith's solder).

Plumber's solder contains 2 parts lead and 1 part tin (for jointing lead).

### CHAPTER XVI

### IRON

Symbol, Fe. Specific gravity, 7.86.

Atomic weight, 55.85. Melting-point, 1505° C.

IRON is regarded as among the most useful of the metals, because of its valuable properties and the readiness of its reduction from the ores. In the arts of construction it is of special value, being the strongest, and at the same time among the lightest and cheapest, of the metals. The three forms in which it occurs in commerce—cast iron, malleable iron, and steel-render it adaptable to many purposes where great pliability, rigidity, and tenacity, are desired. The metal is very widely distributed over the earth, being found in clay, rock, and sand, and in the form of various ores, and occasionally, as in meteorites, in the metallic state. It occurs native in minute traces in basalt and lavas, as spicules. iron occurring in basalt and lavas is known as "telluric iron "; that in the meteorites as "meteroic iron," from its supposed meteoric origin.

Iron is most frequently found combined with other metallic or chemical compounds, in which condition it is found combined with sulphur, oxygen, phosphorus,

and carbon.

Meteoric Iron.—Meteoric iron has been found to contain traces of cobalt, nickel, copper, manganese, sulphur, etc., the presence of the nickel to the extent of I to 2 per cent., and the characteristic markings of Widmanstätten being peculiar to this iron. To produce

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these markings the iron may be planed and polished, and the surface etched with dilute nitric acid. They are most frequently crystalline, or appear as parallel strize or as rhombic folize, with the spaces between the markings slightly raised, showing that the nitric acid has etched the surface by dissolving out some of the components of the meteoric iron in a regular manner as they occur in the ore. At Ovifak, on the island of Disko, off the coast of Greenland, fifteen masses of meteoric iron were found, the largest of which weighed 21,000 kilogrammes,\* while others of considerable weight have been found in Mexico,† Africa, Hungary, etc.

### Occurrence-

Ore,	Formula.	Iron per 100 Pts. of Pure Ore.
Magnetic iron ore, or magnetite Red hæmatite, or specular iron ore Brown hæmatite, or limonite ,,,,, or turgite Spathic iron ore, or siderite Iron pyrites, or fool's gold Clay ironstone, or argillaceous iron ore Blackband iron ore	$\begin{array}{c} {\rm Fe_3O_4} \\ {\rm Fe_2O_3} \\ {\rm 2Fe_2O_3.3H_2O} \\ {\rm Fe_2O_3.H_2O} \\ {\rm 2Fe\cdot O_3.H_2O} \\ {\rm FeCO_3} \\ {\rm FeS_2} \\ \\ \hline$	72 70 60 48 46 17 to 50 21 to 43

These are the chief sources of iron for industrial purposes; the formulæ as given will denote roughly the

composition of the ores.

Magnetic Iron Ore.—Is the richest and one of the most widely distributed sources of iron. This ore, one variety of which constitutes the loadstone, is so called from its power to attract steel, and is capable of rendering steel magnetic. It is generally found in large masses, and mostly in Northern countries, as Norway, Sweden, Russia, and North America. A variety occurs which

<sup>\*</sup> Roscoe and Schorlemmer. † Huntingdon and Macmillan.

contains considerable quantities of manganese and zinc oxides, and is known as "Franklinite."

Red Hæmatite.—Derives its name from the bloodred colour which the ore posesses. It occurs in large masses, hard and shining, in forms varying from the kidney-like ore of Cumberland to bundles of fibres. It is found in abundance in Cumberland, Lancashire, Glamorganshire, Lake Superior, Spain, and Algeria, and is more abundant than the magnetic iron ore. It consists essentially of anhydrous ferric oxide. Red ochre is a soft variety of red hæmatite combined with clay.

Brown Hæmatite.—Is of practically the same composition as the red hæmatite, only containing from 10 to 15 per cent. water of hydration. It occurs as globular masses, as grains, as stalactites, as beds and veins. Yellow ochre is a variety of brown hæmatite. This ore is found in Cumberland, France, Spain, Northamptonshire, Lincolnshire, and Gloucestershire.

Spathic Iron Ore.—Consists chiefly of carbonate of iron, mixed with various foreign matters. Occurs combined with manganese, which renders it of special value for the production of certain steel-making alloys. It is found in Saxony, Durham, Styria, and Carinthia.

Iron Pyrites.—Contains iron and sulphur, and is largely used as a source of sulphur in the manufacture of sulphuric acid, the sulphur having been removed, and any traces of copper extracted. The remaining ferric oxide is reduced to the metallic state.

Clay ironstone and blackband are found mainly associated with coal, limestone, shale, and clay, and occur in Britain, Belgium, and Silesia.

Reduction.—Iron is used in three principal forms, the properties of which vary according to the percentages of carbon contained. Thus, we have cast iron, containing 1.5 to 4.5 per cent.; malleable and wrought iron, 0.15 to 0.3 per cent.; and steel, from 0.1 to over 2 per cent. of carbon. From these three varieties we have all the various preparations of the metal.

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**Cast Iron** is the metallic product of the blast-furnace, and is the variety from which malleable iron and steel are generally prepared. It is obtained from the ore by smelting, with the addition of suitable fluxes. The types of furnaces vary, but the most commonly used type for the reduction is the blast-furnace.

The production of pig or cast iron from the ores of iron comprises two principal stages—i.e., the preparation of the ores and the smelting.

The ore is prepared by submitting it to a roasting or calcination which expels water, carbon dioxide, sulphur, and other volatile substances. The process also'leaves the ore in a more porous condition, and in a state more easily permeated and acted upon by the reducing gases of the blast-furnace. The calcination also converts any ferrous oxide present into ferric oxide, which does not readily combine with silica or form fusible compounds in the furnace. The ore is smelted by mixing with a quantity of fuel to act as a reducing agent, and to develop the necessary temperature within the furnace. It is also necessary to add a flux, in order to combine with the impurities of the ore to form a fluid slag. The fuel mostly used is hard coke, although in districts where the coal is non-coking it is used in the raw condition. flux used is practically always limestone, although sometimes quicklime is used, and very occasionally an aluminous material is added. The proportions of fuel and flux added to the charge depends upon the richness and purity of the ore being smelted. The mixture of fuel and ore is charged through an opening in the top of the furnace. The fuel is kindled, and air under pressure is forced into the furnace through nozzles or blowpipes called the "twyers," which are placed round the furnace near the hearth. The twyers vary in number, from six in small furnaces to twelve or fourteen in very large furnaces. The air for the combustion is in modern practice nearly always heated by passing it through stoves, which are heated by the waste gases of the furnace. In this way a large quantity of heat which would otherwise be wasted is utilized, and a very considerable economy of fuel effected. The oxygen of the air, entering the furnace, acts on the carbon of the fuel, and is immediately converted into carbon monoxide; any small quantities of carbon dioxide formed are immediately converted to carbon monoxide by combining with an additional quantity of carbon. This carbon monoxide now acts upon the ferric oxide of the ore, with the production of carbon dioxide and metallic iron. As the fuel burns away in the lower portions of the furnace, developing a very high temperature, the whole charge gradually sinks in the furnace, the reduced iron melts and runs down into the bottom portion or crucible, the flux combines with the siliceous matter and gangue of the ore, forming a slag which melts and also runs down to the hearth, and remains in a fluid condition on top of the molten iron, as it is of a lower specific gravity. When sufficient has been accumulated, the iron and slag are run off or "tapped" through holes provided for the purpose. The iron is run into sand or iron moulds, and when cold presents the familiar appearance of pigs. The iron contains about 3.5 to 4.5 per cent. carbon, which has dissolved through contact with the fuel; also varying quantities of silicon, sulphur, phosphorous, and manganese.

The pig iron produced may be of two varieties, known

as white iron and grey iron.

White iron contains nearly the whole of the carbon in chemical combination with the iron. It is usually produced in furnaces charged with the minimum quantity of fuel. Sudden cooling of the molten metal will also cause the carbon to be in combination, and thus produce white iron. White iron is very hard and brittle.

Grey iron contains the greater portion of the carbon in the uncombined or free state as graphite. It is produced in furnaces charged with a large proportion of fuel. Slow cooling of the metal produces grey iron, which is IRON . 143

soft. The carbon separates from its chemical combination, and frequently a certain amount of graphite can be removed from the surface of the metal. Grey iron contains a considerable amount of silicon, which induces the crystallization of the carbon as graphite. White iron is principally used for the production of malleable iron. Grey iron is used for foundry purposes and for steel-making. The grades of grey iron rich in graphite are mixed with poorer grades when used for castings. Grey iron is a little less fusible than white iron. Cast iron contains from about 2.0 to 4.5 per cent. carbon. By using ores containing a large quantity of manganese in the blast-furnace, various grades of manganiferous pigs can be produced. The manganese enables the iron to hold more carbon than normal pig. the alloy having a crystalline structure with a lustrous fracture, and known as "spiegeleisen," which contains from 5 to 20 per cent. manganese and 4 to 6 per cent.

The fact that grey iron is converted into white iron by rapid cooling is made use of in the production of chilled castings. The molten grey iron is poured into massive iron moulds at those portions of the castings that are to be chilled. The surface immediately in contact with the iron mould is converted into hard white iron of a depth of, say,  $\frac{1}{8}$  inch.

Malleable Cast Iron is produced from white pig iron, and is largely used for small articles, such as spanners, keys, bolts, and parts of machinery, where a strong ductile material is required, but where the cost of forging would be prohibitive. The articles are cast from white iron into moulds prepared in sand in the usual way, and afterwards submitted to an annealing process. The articles are packed into iron boxes or pots with finely powdered hæmatite ore. The boxes are then placed into an annealing furnace, and gradually heated to a temperature of about 1,000° C., and maintained at that temperature for from three to ten days, depending upon

the size of the castings. During this heating a large proportion of the carbon is removed from the iron by oxidation; the remaining carbon is converted into a special form of graphite or free carbon, which is disseminated throughout the mass. A method of producing malleable cast iron, largely used in America, consists in heating the white castings in some inert material, such as sand or bone ash, instead of iron ore. The carbon is not reduced in this method, but the whole of it is precipitated in a finely divided form of graphite. This process is known as the "black-heart process," from the fact that the fracture of the material has a black velvety appearance. It is claimed that this method gives superior results in the case of large castings. Malleable cast iron is softer, tougher, and more ductile, than ordinary grey castings. The tensile strength is also very greatly increased.

Malleable or Wrought Iron may be produced from cast iron, either by what is known as "dry puddling" or by "pig boiling." In the former process the charge is never perfectly fluid, only reaching a pasty consistency, whilst in the latter the charge is completely liquid

during the refining.

In the original process as invented by Cort, white iron was always used, and the bottom of the furnace was lined with sand, the iron remained in a pasty condition; a certain amount of the iron was converted to oxide of iron by the action of air, and the whole mass had to be vigorously stirred to mix the oxide of iron formed with the pasty metal. The impurities were thus removed by oxidation, chiefly by the oxides formed during the melting, and a considerable waste of iron occurred.

In working this process, grey iron could not be used,

unless it was first converted to white iron.

The modern or wet method (pig boiling) for the manufacture of malleable iron differs from the dry puddling process, inasmuch as the bottom of the furnace is lined with an oxidizing material, such as hæmatite, hammer

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scale, or cinder produced in the later stages of the process. Grev iron is used without previous conversion to white iron. The charge of iron is placed into the hot furnace, upon the bottom of which has been previously spread the oxidizing material. The metal is melted, and allowed to become perfectly fluid before incorporating the oxide of iron. During this incorporation of oxides, the temperature of the furnace is somewhat reduced; slags containing oxides of iron are added in order to combine to form a flux with the silica formed by oxidation of the silicon contained in the pig iron. The carbon is also attacked by the oxides, and carbon monoxide is formed, and escapes through the slag, burning with a blue flame. The escape of CO also causes an ebullition in the mass. At this stage the temperature of the furnace is again raised, to compensate for the increased viscosity of the metal which occurs as the impurities are removed. The charge is well rabbled until the ebullition ceases and the metal comes to nature. The metal is then agglomerated into lumps or balls, which are brought to welding heat, removed from the furnace, and hammered into blooms. The hammering expels the slag from the metal, which is then rolled into bars or other sections desired.

## Steel may be produced by—

1. The cementation process.

2. The crucible or pot process.

3. The Bessemer or pneumatic process.

4. The open hearth processes.

It is by these four methods that practically all the steel which is used at the present time is produced.

Cementation Process.—This process was at one time in general use for the manufacture of a large proportion of tools and cutlery steel, but it is now chiefly used for producing cement bar for remelting in crucibles for the manufacture of "cast steel." Best Swedish iron, known as "Walloon bar," is used in the form of flat bars.

These are packed in charcoal in fire-clay pots or boxes, which are hermetically sealed so as to exclude the air. These boxes form an integral part of the cementation furnace, and are set over a long grate. The temperature of the furnace is gradually raised to a bright red heat, and maintained at it for a period of seven to fourteen days, according to the content of carbon required in the finished steel. The carbon is gradually absorbed, and penetrates the mass of iron, converting it into steel. The furnace is allowed to cool for a number of days, and the bars withdrawn. The bars when removed from the pots are covered with blisters—hence the name "blister steel." The bars are made into bundles or "faggots," heated to welding temperature, and hammered. This product is known as "shear steel"; if the bars are doubled on themselves and again welded, the product is "double shear steel."

Crucible or Cast Steel.—Blister steel is not sufficiently regular in composition and texture for the very finest quality of tools and cutlery; the carbon gradually decreases from the outside to the centre. This is the case even after several pilings and weldings. The better way of obtaining a homogeneous and uniform product is to cut the blister bars into small pieces, and to melt in crucibles. The metal after complete melting is kept at the highest temperature of the furnace for about fifteen minutes, to what is known as "kill" the metal. This causes an evolution of the dissolved gases and oxides from the metal, and so allows it to be cast into sound ingots. Killing may be dispensed with if a small amount of aluminium is added to the metal before pouring.

The crucibles employed are made of a refractory clay, and are heated either in a coke-hole or gas-fired furnace. The metal is then cast into ingots, and is known as "crucible cast steel," which is afterwards reheated, hammered, and rolled to a desired size and section.

The Bessemer Process consists in blowing air through

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molten pig iron, by which means the various impurities are successively oxidized and removed, the result being practically pure iron, which is then recarbonized by the addition of material rich in carbon, such as pig iron or spiegeleisen, according to the temper of the steel required. The operation is carried out in a pear-shaped vessel known as a "converter." This consists of a shell of steel plates lined with a refractory material, and supported on trunnions, on which it can be rotated for the purpose of filling or emptying. A blast of air is supplied from a blower, through pipes which pass through the trunnions to the wind-box at the bottom of the vessel, and thence by twyers to the metal. The usual size of converter holds a charge of 10 to 15 tons of metal.

In the original Bessemer process, the converter was lined with ganister, a very siliceous, refractory material. This is still the case in what is known as the "acid process." Iron containing phosphorus in considerable quantities cannot be employed in the acid process, as phosphorus can only be eliminated in the presence of a strong base capable of combining with the phosphoric acid produced by its oxidation to form a stable phosphate. Hæmatite pig iron has therefore to be employed in an acid-lined converter.

The process is carried out as follows: The converter is first heated strongly by a coal or coke fire, the ashes cleaned out, and the vessel turned down to a horizontal position. The necessary amount of pig iron is poured in, the blast put on, and the vessel raised to a vertical position. The silicon and manganese are at once attacked by the oxygen of the air, forming silica and manganese oxide, with evolution of heat. The oxide of manganese, together with some oxide of iron produced, combines with the silica, forming a slag consisting of manganous and ferrous silicate. As the silicon and manganese are removed, the carbon of the metal becomes attacked, being converted to carbonic oxide; the charge of metal boils from the escape of carbon monoxide,

which burns at the nose of the vessel with a long flame, and at the same time sparks of burning iron particles are emitted. As soon as all the carbon is removed the flame disappears, and the vessel is turned down, necessary additions of spiegeleisen made, and the metal poured into ladles, and then turned into the moulds. In the basic Bessemer process the converter is lined with a basic material, such as dolomite or magnesite. The procedure is the same as in the acid process, up to the point where the carbon is removed—drop of the flame. At this stage, instead of immediately turning down the vessel, the blowing is continued for several minutes longer, and additions of lime are made. It is during this period, known as the "after-blow," that the phosphorus is removed, as phosphoric acid, which combines with the lime to form a stable phosphate of lime. When the phosphorus is all removed, the vessel is turned down, the slag poured off, and the necessary additions made, and the metal is then cast into ingots.

The Open Hearth Process.—Steel can be produced by refining pig iron on the open hearth as well as in the converter. The process is usually carried out in gasfired regenerative reverberatory furnaces. There are two principal forms of the open hearth process, known respectively as the "Siemens" and the "Siemens-Martin" process. In the former pig iron and iron ore are used, whilst in the latter a mixture of pig iron and steel or wrought iron scrap is employed. In general practice at the present time a combination of these two is usually adopted. In the Siemens process the purification of the pig iron is effected by oxidation by means of

the iron ore and the furnace gases.

In the Siemens-Martin, the removal of impurities is effected by dilution with the scrap, and selective oxidation by the furnace gases.

The process may be worked either acid or basic, as in the case of the Bessemer, the acid furnace being lined IRON ' 149

with silica, and the basic with dolomite or magnesite. The capacity of the open hearth furnaces varies from 5 to 200 tons. The furnace is heated to a high temperature, and pig iron and scrap charged in; the iron melted and iron ore thrown into the bath from time to time, until all the carbon, silicon, and manganese are removed to the desired extent.

When working a basic furnace, a pig iron high in phosphorus may be used, and lime is added to the bath to combine with the oxidized phosphorus. The complete removal of the carbon should not be effected before the phosphorus is oxidized, as it is necessary to keep the metal on the boil, or the last portions of phosphorus are very difficult to remove. Small samples are drawn from the bath from time to time as the process proceeds, and are examined by appearance of fracture to determine the amount of carbon and phosphorus in the metal. These samples are also occasionally analyzed for carbon and phosphorus. When removal is sufficiently complete, additions of spiegel or ferromanganese are made, and the metal tapped into the ladle, and then cast into ingot moulds. The open hearth process is possibly the one now most largely used, and also produces the best quality of steel in large quantities. The bath of metal is completely under the control of the. melter, so that steel of uniform quality can be regularly obtained.

**Properties of Iron.**—Pure iron is only prepared as a chemical curiosity, and is a white lustrous metal capable of taking a high polish. It possesses a higher fusing-point than malleable iron, and is soft, ductile, and tenacious.

Cast iron is the most impure form of iron, generally containing sulphur, phosphorus, manganese, silicon, etc. The total impurities are generally about 8 to 10 per cent. It possesses the lowest melting-point, 1,200° C.; is lowest in tenacity, ductility, and elasticity. It can be hammered, rolled, and forged, if raised almost to fusing-

point, when it becomes plastic. Cast iron cannot be tempered, and so is useless for edge tools. Malleable iron is the purest form of iron used industrially, having the lowest percentage of carbon. It is fibrous in structure, and, as its name denotes, is malleable, ductile, and elastic. It is also known as "bar" or "wrought" iron. Malleable iron cannot be tempered. Two pieces of this iron, if heated, may be forged or welded together,

a property of great value and importance.

Steel is the most important alloy of iron from a dental standpoint, and contains o. I to over 2 per cent. of carbon. It ranks as one of the strongest and most elastic of the metal group, these properties and its comparative lightness being important where weight is of consequence, as in the making of forceps, elevators, pliers, etc. It can also be brought to a fine edge, having the edge improved in hardness and durability by tempering. In wire (piano wire) form, steel is made use of in correcting cases of malocclusion, etc., its great strength and elasticity being most valuable. In sheet form it is used in the making of clamps, matrices, etc. Steel oxidizes or rusts rapidly when in contact with moisture, and is best protected by a plating of nickel, silver, or gold. Steel wire will not adhere to vulcanite unless it has been coated with a thin layer of tin. This is effected if the steel is moistened and coated with bluestone (copper sulphate), the deposit of copper causing the tin to adhere more readily. The hardness of steel is much affected by the percentage of carbon present; the larger the quantity of carbon, up to a certain limit, the harder and more brittle the steel. Industrially, steel is assuming more importance when alloyed with other metals, whereby its physical properties are greatly modified.

Effects of Impurities in Iron.—Silicon, in the absence of carbon, hardens iron, and if present in large quantities, renders it brittle. In iron containing much carbon, silicon softens iron. Sulphur if present in large amounts

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causes red-shortness. The addition of ferromanganese reduces to some extent the effects of sulphur, and also acts as a deoxidizer.

Arsenic causes cold-shortness only less markedly than phorphorus.

Phosphorus in the same quantities produces cold-

shortness.

## Alloys of Iron.

Tungsten Steel.—Tungsten added to steel greatly increases the hardness; indeed, steel cannot be hardened further unless by being heated to redness and plunged into oil, and even then the higher alloys almost invariably crack when wrought upon. Tungsten steel is largely used for machine tools, as a much greater cutting speed can be used without drawing the temper than is possible with carbon steel. These alloys generally contain from 2 to 7 per cent. of tungsten; they are sometimes referred to as "self-hardening" steels, and also as "Mushet" steels.

Tungsten added to steel from 2 to 3 per cent. increases

its power to retain magnetism.\*

Chrome Steel.—This alloy generally contains from 0.25 to 2 per cent. of chromium. Chromium added to steel increases the hardness, elasticity, strength, and extensibility. An excess makes the alloy very brittle. It is used chiefly as a sheathing for projectiles. Chroming increases the hardening capacity of the steel by sudden cooling.

Aluminium Steel.—This alloy must not contain more than I per cent. of aluminium. Aluminium added to higher grade steel in small quantities causes it to cast better, overcomes red-shortness, increases elasticity and tenacity, and reduces oxidation; it has no effect on the melting-point, and if added to excess, makes steel

brittle and increases crystalline structure.

Nickel Steel.—This alloy contains from 2 to 45 per cent. nickel, and from 0.2 to 0.3 per cent. carbon. It

<sup>\*</sup> Huntingdon and Macmillan.

has a higher elastic limit, and corrodes less in sea-water than ordinary steel. When "Harveyized," it is much used for armour-plating, gun-barrels, and projectiles. French smelters add from I to 2 per cent. of nickel to form this alloy. The alloy known as "invar steel" contains about 35 per cent. nickel, it is non-magnetic, and shows practically no change in dimensions with change of temperature.

Copper Steel.—In this alloy there may be as much as 20 per cent. of copper. Copper increases tenacity, strength, and malleability, which are further increased

if the alloy is tempered.

Manganese Steel.—The addition of not less than 6 per cent. and not more than 14 per cent. of manganese increases the toughness and tenacity of steel, and reduces its strength and ductility; more than 14 per cent. produces a diminution in ductility.

Silicon Steel.—This alloy has properties similar to those of aluminium steel, and the silicon and aluminium are in almost similar quantities in the respective alloys.

The silicon slightly increases tenacity.

Tempering of Steel.—Steel is generally forged or shaped while in the soft state, the tempering or hardening being done, especially in the case of dental and surgical instruments, when the metal is ready for plating. The method employed varies with the instrument to be tempered. The process generally consists in raising the steel to the desired heat, then plunging it into water. salt and water, oil, or mercury. Finely tempered instruments, such as clamps, burs, fine enamel chisels, etc., should not be exposed to the naked flame, but coated with fat or soap, enclosed in a case surrounded by carbon. or heated on a sheet of iron embedded in sand. For new instruments, such as scalers, excavators, etc., the best results are obtained by heating the entire instrument to a full red heat, and plunging into water, then tempering according to the colour which moves in front of the flame or heat. The following table gives the

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temperatures corresponding approximately to the various tints to produce the best cutting edges.

Temp.	Colour.	Temper.
22I 232	Very faint yellow Pale straw	Lancets, enamel chisels, etc. Razors and fine surgical instruments generally.
243 254 266	Full yellow Brown Brown with purple	Excavators, penknives. Pluggers, gum scissors. Pocket-knives, axes, etc.
277 288 294 316	spots. Purple Bright blue Full blue Dark blue	Table-knives, metal shears. Watch-springs, swords. Augurs, fine saws. Pit and hand saws.

Case-Hardening of Steel.—Articles to be hardened are packed in airtight cases surrounded by some carbonaceous material, such as leather, bone dust, hoofs or horns, etc., with a little soda or lime. The box and contents are gradually heated to redness, and maintained at this heat for a time depending on depth of case-hardening required.

Superficial hardening is obtained by dipping red-hot iron into prussiate of potash, and then plunging into cold water. Case-hardening is employed where friction is to be resisted, for lathe-heads, engine bearings, etc., and imparts to the metal an extremely hard skin, which resists metal files. The process is also employed for

hardening armour-plates.

Harveyizing of Steel.—This is a modification of the cementation process, whereby the outer thickness of a mild steel plate is caused to take up an additional percentage of carbon, and so acquires increased power to resist penetration. The steel to be Harveyized is laid in chests on a furnace bed of fire-bricks and sand; carbon is tightly packed around it, and the chests are covered with fire-bricks. The temperature is raised to about

1.200° C., and retained at this heat until the steel has absorbed 1 per cent. of carbon; and the carbon having having penetrated as far as is required, the furnace is allowed to cool slowly. The steel produced is extremely hard on the surface, while it still possesses the properties of toughness and ductility in the interior.

#### CHAPTER XVII

### **ALLOYS**

WITH the exception of gold, platinum, and aluminium, there are few metals used in dental metallurgy in the pure state; the metals used are generally in combination with one or more metals, this combination being known as "alloying." Metals as a rule are too soft for general purposes when in the pure state; therefore they are alloyed or mixed with another metal or metals to increase the hardness. The cost of such metals as gold, platinum, and iridium, also leads to their being alloyed, to reduce cost of production. The results of alloying generally are best studied if the effects on the general physical properties are considered.

## Physical Properties of Alloys.

Hardness.—Alloys generally are harder than any of the metals composing them. Examples: The alloys of gold, silver, and copper, as in the reduction of the carats of gold; the gold and platinum alloys used for clasps, etc.; copper and tin, as in the bronze alloys, the alloy possessing great hardness, and, in some of the old specimens used for weapons, good edge strength.

Fusibility.—Alloys generally possess lower meltingpoints than the metals composing them. Examples: The reduction of the carat of the gold reduces the meltingpoint; the group of fusible metals. Wood's fusible metal is composed of bismuth, lead, tin, and cadmium, and melts at 71° C.; while the lowest fusing-point of the

component metals is tin at 232° C.

Colour.—The colour resulting from an alloy is generally what would be expected—namely, a mixture of all the colours contained in it.—Examples: Silver added to pure gold whitens the gold; copper added to gold reddens it; hence, in alloying gold, the metals silver and copper are nearly equally balanced in quantity, the one overcoming the effect of the other on the resulting colour. While this is true generally, there are some notable exceptions. For instance, if 39 parts of gold are added to II parts of aluminium, an intensely ruby-coloured alloy results; equal parts of copper and antimony yield a violet-coloured alloy known as "the regulus of Venus"; while zinc and varying proportions of lead and tin added to copper yield alloys of various shades of velvety brown.

Density.—Alloys seldom possess specific gravities equal to the mean density of the metals combined in them. Expansion of an alloy on setting reduces the density, as, for example, in the union between gold and silver, gold and copper. Again, contraction on setting increases the density, as is seen in the union between gold and tin, gold and zinc, silver and tin, copper and tin, and

copper and zinc.

Specific Heat.—The specific heats of alloys are generally the mean of the specific heats of the constituent metals.

Malleability and Ductility.—These properties are powerfully influenced by alloying, the result generally being a decrease in one or both of these properties. The malleability and ductility of an alloy, however, cannot be reckoned from the mean average possessed by the constituent metals of the alloy. For example, gold, a soft metal, alloyed with a trace of lead, another soft metal, yields an alloy which is brittle and unworkable. Again, gold, platinum, silver, and copper, all soft and malleable metals, yield alloys whose malleability and ductility are generally less than that of the metals when unalloyed. The best selected copper, alloyed with  $\frac{1}{1000}$  part of antimony, is converted into the worst conceivable.\*

<sup>\*</sup> Sir Hussey Vivian.

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The effect of alloying generally being to increase the hardness, the malleability is correspondingly reduced.

Tenacity.—This property is generally increased by alloying, the results in some cases being remarkable, and bearing no relation to the mean average of the metals alloyed.

Mathiessen's table, drawn from experiments made with wires of the same gauge, and made to withstand the same strain before and after alloying, gives as follows:

UNALLOYED.			ALLOYED.		
			Pounds at Rupture.	Pounds at Rupture.	
Copper			25 to 30	Copper plus 12 per	
Gold			20 ,, 25	cent. tin 80 to 90	,
Silver			45 ,, 50	Gold plus copper 70	
Platinum	1		45 ,, 50	Silver plus platinum 75 to 80	,

Conductivity.—This property in alloys is generally much below that of the pure metals. For example, copper with an addition of silver has its power of conducting heat and electricity much reduced, even although silver stands very high in this property; while the addition or presence of a small quantity of bismuth causes copper almost entirely to lose this property. Again, pure gold, when inserted as a filling, conducts thermal changes with great rapidity to the pulp tissue. This property is very much reduced when gold is alloyed with such metals as silver, copper, and tin, and amalgamated; or when the gold is inserted as thin ropes of foil intermixed with tin-foil. Although this last combination is not introduced as an alloy (it being understood that some form of fusion or intermingling of the metallic molecules is essential in the formation of an alloy), the tin in this instance exerts its lower conducting power even when in contact with gold.

Expansion by Heat.—Alloys when heated generally expand in a degree very closely approximating to the ratio of the relative volumes of their constituents.

Oxidation.—Alloys are generally more readily oxidized than their constituents. This is seen, for example, in the

various carats of gold. Aluminium, on the other hand, is capable of exerting peculiar influences; added to steel and iron, it reduces the rapidity of oxidation, as also do nickel, tungsten, cerium, etc. Zinc as used for dies oxidizes rapidly if overheated, even when brought to melting-point frequently; but the addition of 10 per cent. aluminium reduces this tendency towards rapid oxidation very considerably. Aluminium itself in the mass has no tendency to oxidize, but in a finely divided condition its affinity for oxygen is extremely great; and if coated with a thin layer of mercury, it oxidizes rapidly, and is soon covered with a white film of alumina, which may be readily detached in flakes. Pure gold and pure platinum do not oxidize at ordinary temperatures; yet the alloys of the metals when worn in the mouth for some time, either as gold and platinum fillings, gold plates, crowns, or clasps, become oxidized superficially.

Decomposition.—Alloys containing volatile metals such as mercury, zinc, antimony, etc., are readily decomposed by heat. Amalgams, for instance, when heated to redness, yield the mercury, etc., and are readily reduced to powder. Other metals which enter into more intimate contact when alloyed are not so readily decomposed. Amalgams will yield nearly all the mercury and zinc if heated to a bright red for some minutes; but where gold is contaminated with lead or alloyed with tin, entire separation by using heat alone is impossible, the addition of potassium nitrate being

necessary to effect this removal.

The copper zinc and several other alloys may be com-

pletely separated by heating in a vacuum.

Sonorousness.—This property is developed by many metals only when alloyed. The bronzes, for instance, possess this property, yet tin, the chief constituent, does not possess it to any extent. Aluminium, though possessing this property only after special treatment in casting, is much improved in sonorousness if alloyed with silver or silver and copper.

Action of Acids upon Alloys.—The action of acids upon alloys generally is to dissolve out the excess of any metals which they attack as single metals, the action, however, generally being more pronounced. Advantage is taken of this in the parting process by sulphuric and nitric acid used in the treatment or purifying of gold. Other alloys, again, such as of silver and platinum, when silver is present beyond the "content" of platinum, are attacked by nitric acid, the platinum passing into the solution, although the acid has no action upon the platinum alone. Each alloy in many ways is best studied for its properties by itself, and the textbook written by the late Sir W. Roberts-Austin, "An Introduction to the Study of Metallurgy," gives much valuable information on the subject, also "Alloys," by Edward F. Law.

From the foregoing it will be seen that alloys as a class present some peculiar properties. When it is remembered that metals are capable of behaving, in all essentials, in the same manner as liquids, these properties will not present the same difficulties. All the metals are solid at ordinary temperatures, with the exception of mercury, which becomes solid only at  $-39^{\circ}$  C. Heated to their fusing-points, they become liquid, and behave while in this state as a liquid, intermixing with another metal or metals, occluding gases, etc. If heated beyond this point, the metals volatilize, passing off as a vapour, in much the same manner as water being converted to steam; and from the vapour they may be recovered again to the metallic state by cooling. This briefly outlines what changes occur with metals as a class.

**Preparation of Alloys**—By Fusion.—Alloys are generally prepared by a process of fusion, and may either be formed simultaneously, or the metal possessing the highest melting-point melted, and the others introduced in their order. It is found, in preparing alloys of pure gold and platinum alloyed with silver and copper, that,

if these metals be melted simultaneously with the gold or platinum, the alloy is melted at a much lower temperature than if the metals were melted separately. This fact is especially useful in preparing alloys of platinum, as they can be prepared by using the ordinary furnace heat, or even using a Fletcher furnace.

In all cases alloys for dental purposes should be pre-

pared from pure metals.

When noble and base metals are to be combined in an alloy, the same rule holds good; and to avoid oxidation the metals should be covered with a layer of powdered charcoal during the heating and melting. Where such volatile metals as zinc and antimony are being added, even although only in traces, the alloy should be allowed to cool to near the melting-point of the volatile metals before they are introduced, the alloy being then well stirred and pouted. The practice of melting alloys under a layer of borax is generally only applicable to those containing noble metals. The action of the ordinary commercial borax upon base metals is to cleanse the mass from oxides by solution or absorption of some of these in the borax glass.

Where alloys are prepared on a small scale, crucibles are generally employed. They should be well tempered before using, and the sides coated with borax and thoroughly glazed before receiving the alloy, as there is loss of metal through some of it passing into the body of the crucible if this is neglected. (See Dental Amalgams)

By Compression.—In alloys composed entirely of base metals, it has been found practicable to prepare these by compression. Professor Walthère Spring, of Liége University, prepared one of the fusible alloys composed of 15 parts bismuth, 8 parts lead, 4 parts tin, and 3 parts cadmium. The metals were finely divided, enclosed in a steel cylinder with an accurately fitting piston of steel, and compressed. The block of alloy so produced was again reduced to powder and again compressed, giving an alloy which melted at

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65° C., the same temperature as that generally produced by fusion, although the lowest melting-point of the constituent metals is that of tin at 232° C. Advantage may be taken of this means of preparing alloys composed chiefly of metals which are either volatile or readily oxidized, as by this means there is absence of loss of weight due to these causes.

Union of Metals by Electro-Disposi ion.—The Japanese bronzes and alloys so largely used for art purposes can be prepared by electrolysis, as can also brass from copper and zinc, from the mixed cyanides of copper and zinc, dissolved in a solution of cyanide of potassium. The process has been successfully employed in the preparation of silver and gold alloys, in the treatment of compound ores, etc.; but so far no literature is available to show that the process has been employed in the preparation of alloys used in industry or dentistry.

# The Constitution of Alloys.

It is the exception rather than the rule for metals to be used in the pure state, as simple metals are unable to meet the very great demands of the modern user of metals. The fact that remarkable changes in properties may be effected by the addition of varying proportions of one metal to another, and the production of alloys, has been known and practised for many centuries. It is possible by alloying suitable metals in the proper proportions to produce a material to fulfil almost any conditions as to strength, ductility, malleability, hardness, conductivity, fusibility, corrodibility, etc.

Although the art of alloying has been practised for so long, it is only within the past twenty-five years that alloys have been investigated systematically. The result of modern research has made it clear that there is a very close relationship between the constitution of an alloy and its properties, and the most fruitful results have

been obtained by considering alloys as solutions of metals in each other.

It is in comparatively few cases that the component metals of an alloy exist in the elementary state. For instance, if an alloy be prepared by melting together gold and lead in about equal proportions, the cold mass contains very little, apparently, free gold; but the greater portion of it is composed of two kinds of white crystalline bodies, which are definite chemical compounds of gold and lead, and in addition to these there is an eutetic having as one of its constituents lead containing a portion of one of the chemical compounds in solid solution. Although only the two elementary metals, gold and lead, are present, yet the alloy contains at least four constituents, and in order to describe it nearly all the principal terms for the constituents of alloys have to be employed. A constituent of an alloy may be defined as a separate body having an entity peculiarly its own.

The constituents of alloys may be—

Free metals in a pure state.

Solid solutions of one metal in another, or of chemical compounds in an excess of metal.

Eutectic mixtures.

Chemical compounds of metals with metals, or of metals with non-metals.

. Allotropic modifications of metals or of compounds.

metallic components which are thrown out of solution, or crystallize in the pure state during cooling and solidification of the molten alloy. If they are formed in a fluid matrix, being the first portion to solidify, they occur either as crystallites or as perfectly formed crystals, with all their true faces and angles (idiomorphic crystals). If the metal has a lower melting-point than that part of the alloy which first solidifies, it is found between the crystallites or crystals filling up the inter-

stices. If an eutectic is formed, one or all of the metals

may be in the free state in juxtaposition.

2. Solid Solutions.—A solid solution is really the cold mass resulting from the cooling and solidification of a molten mixture of metals, whose state of mutual solubility remains unaltered by the process of solidification, and the alloy remains a solution on crystallization. In other words, the crystals of which the solid mass is composed have each the same average composition as the molten liquid.

A solid solution may be considered as a solid substance containing two or more elements in such an intimate mixture that they cannot be detected even under

the highest powers of the microscope.

There are some metals which do not remain either wholly or partially in solution on solidification, and to such solid alloys the term "solidified solution" is sometimes applied. It is important that, in order to avoid confusion, the distinction between "solid solution" and "solidified solution" be noted. The crystalline form of solid solutions is usually, if not identical very nearly that of the constituent which is in excess.

There are several kinds of solid solutions which may be found in alloys—viz.:

(1) In which one metal on crystallizing retains a portion of the other uniformly diffused through its entire crystalline mass.

(2) In which during crystallization the external boundaries of the crystals contain more of the dissolved metal than the interior.

(3) In the case of metals forming definite compounds a portion of the compound is retained in solution in the excess of metal or metals.

(4) In which the non-metallic elements form chemical compounds with a portion of the dissolving metal, and remain in solid solution. As all metals and alloys are made up of aggregates of crystals, solid solutions of one

or more metals in others must be regarded as crystalline solid solutions.

3. Eutectics.—Dr. Guthrie in 1884 published the results of an interesting research upon the changes which take place when alloys pass from the fluid to the solid state. He showed that the solidification of a molten alloy was closely analogous to the solidification of molten granite. In the case of the latter the felspar and quartz crystallize out, leaving still fluid the mica, and in the case of an alloy certain of its constituents crystallize out, until the mixture of maximum fusibility is left as a kind of "mother liquor." Guthrie called this mixture of maximum fusibility the "eutectic alloy." It is clear that he recognized that the eutectic proportions of the metals present have not necessarily any relation to their atomic weights, for he says: "Of course, in many cases metals can be fused together in simple multiples of their atomic weights, but in most such cases one of the metals will separate out first, and so destroy the ratio." "When we are dealing with metals which, like antimony or arsenic, are themselves halogenous, on the one hand, or with such strongly chemico-positive metals as sodium on the other, we may and do get alloys of atomic composition, or metallo-metallic salts. But the temperature of fusion of these is never, so far as I am aware. lower than that of either (both) of the constituents: they are not entectic."

The last sentence makes it clear that Guthrie regarded as an essential property of an eutectic that its meltingpoint be lower than that of the mean of the separate constituents.

Guthrie prepared eutectic alloys by melting the metals, allowing to cool so that the metal in excess could solidify, and, when the greater part of the mass had become solid, pouring off the residual alloy which remained as a kind of "mother liquor," and allowing it to set. This crude eutectic was remelted, allowed to partially solidify, and the mother liquor again poured

off. This was repeated until the composition of the mother liquor remained constant. The eutectic may therefore be considered as the solidified mother liquor, and it must possess the following characteristics:

(1) A solidifying and melting point lower than that

of the mean of its constituents.

(2) A single solidifying and melting point.

(3) It may consist of two or more metals which do not unite chemically, or of a metal and a chemical compound, and possibly of two or more definite compounds.

(4) It may consist of a mixture of a free metal and

of a solid solution.

(5) It may consist of a solid solution of a compound in a metal, and the same compound in the free state.

(6) It may consist of two solid solutions.

(7) Is an exception to the general rule, and relates to the eutectic which is formed in solid steel when it cools slowly from above about 700° C. The mass is a solid solution at about 700° C., but splits up into two constituents on cooling. This is usually termed an "eutectoid," to indicate that it has been formed from the solid state.

(8) An eutectic may contain an eutectoid and an eutectic, one formed in the solid state juxtaposed with another formed at its solidifying-point. White hematite pig-iron high is carbon is an example of this.

All eutectics show a duplex structure under the microscope, but they do not all have the same form. In some cases the constituents consist of curved plates in juxtaposition, as in the alloys of silver and copper, and in slowly cooled steel. A common form is the cellular or honeycombed, as in the gold-lead, bismuthtin, and iron-phosphorus alloys. The two constituents sometimes consist of flat plates, as in silver and lead alloys. Some eutectics, if allowed to cool very slowly, assume geometrical crystalline forms. Examples of this are found in lead-antimony, gold-lead, bismuthtin, and antimony-tin-lead alloys.

4. Definite Chemical Compounds.—Many of the metals combine chemically in atomic proportions. They also combine in the same way with certain of the non-metals. They are usually termed "definite chemical compounds," and correspond with the metallo-metallic salts of Guthrie. The eutectics are definite mechanical mixtures, and consist of two or more separate constituents, so that they are distinct from compounds, which are quite homogeneous, and are recognized by possessing characteristics different from those of the elements alloyed. In many cases heat is evolved when metals are brought together in the molten condition, an almost certain indication of chemical union. Iron and phosphorus, copper and aluminium, are examples.

Aluminium and gold form a purple-coloured compound; copper and antimony form two compounds, one purple in colour, and the other very pale yellow; whilst zinc with phosphorus and arsenic forms white compounds.

Aluminium and copper are both what might be considered comparatively weak metals. One is of a neutral grey colour, the other a red; yet they form a compound of golden colour, which is harder, stronger, and tougher than either element.

Copper and zinc forms several compounds. As a general rule the compounds are distinctly harder than either constituent.

Allotropic Modifications.—It is well recognized that some metals can exist in more than one condition, each modification being stable only between certain limits of temperature. The same phenomenon is exhibited in the alloys of such metals, although less marked.

Some chemical compounds can also undergo polymorphic changes. In the case of both metals and compounds, changes in the nature of the constituents only take place if cooling through the transformation temperature is very slow. Many of the alloys containing cobalt, nickel, iron, etc., undergo allotropic changes at certain temperatures.

Alloys of tin and lead containing between 8 and 63 per cent. tin: The change occurs at 149° C. in alloys containing over 18 per cent., and at lower temperatures in those containing less than that amount of tin.

Allotropic changes occur in the compounds of gold and lead (Pb\_Au), cobalt and arsenic (Co<sub>5</sub>As<sub>2</sub>,Co<sub>2</sub>As,

Co<sub>3</sub>As<sub>2</sub>), after solidification.

### Classification of Alloys.

It has already been shown that many metals combine in certain simple proportions to form compounds, having properties different from those of the constituent metals. In some cases these chemical compounds can be isolated, but in other cases, although combination is known to occur, the instability of the resulting compounds prevents their isolation in the pure state.

It has also been demonstrated that other metals do not form compounds, but exhibit various degrees of solubility and admixture; consequently a study of the constitution of such alloys involves only a consideration

of the solubility conditions of the components.

The latter class represent the most simple type, and

for that reason are considered first.

The alloys are usually regarded as solutions, and the most rational method of classification is that based upon the degree of solubility of their component metals.

Considering the mutual solubility of the liquid metals, three possibilities are presented. The two metals are at the moment when solidification is about to commence:

I. Completely soluble in each other in all proportions, and for all concentrations form a single homogeneous liquid.

II. Partially soluble, and between certain limits of concentration form two conjugate liquid solutions.

III. Completely insoluble in each other, and form two distinct liquids for all concentrations.

These may be subdivided by considering the solubility conditions of the metals at the temperatures when solidification is just completed, which may be in the case of Class I.

I. Quite insoluble in each other, and the alloys show two constituents for all compositions.

2. Partly soluble in each other, and the alloys show two constituents between certain limiting compositions.

3. Perfectly soluble in each other in all proportions, and the alloys consist of only a single constituent for all

compositions.

In the case of Class II. it is possible to make Subdivisions I and 2 only, as metals which are only partially soluble in the liquid state are not likely to show complete solubility when solid. Similarly all the alloys of Class III. must be included under Subdivision I.

The alloys in which chemical compounds are formed represent a more complex case, as it is necessary to consider not only the conditions of mutual solubility existing between the component metals, but also the solubility conditions existing between the compound or compounds and each of the metals.

The alloys of these types may be classified according to the mutual solubility of the compound and the component metals when the alloy is just about to begin solidifying. Here, again, there are three main classes:

I. The compound is soluble in all proportions in each of the metals, and the liquid alloy at all concentrations

is a single homogeneous solution.

II. The compound partially dissolves in each of the metals, and between certain limits of composition two conjugate solutions are formed in the just liquid alloy.

III. The compound is insoluble in each of the metals, and the just liquid alloy of all compositions consists of

two conjugate solutions.

Subdivisions based upon the mutual solubility of the compound and the solid metals is again possible thus:

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r. The compound may be insoluble in each of the metals in all proportions.

2. Partially soluble in each of the metals.

3. Completely soluble in each of the metals.

As in the case of alloys forming no compounds, Subdivisions I and 2 can only be made for Class II., and only Subdivision I for Class III.

In the case of alloys in which compounds are formed, certain complications arise in so far that a series of alloys may belong partly to one and partly to another class, as the compound may dissolve completely in one metal in the liquid or solid state, and only partially, or not at all in the other.

It is also necessary to distinguish between systems in which the compound has a definite melting-point, which is the same as that of a mixture of the same composition, so that liquefaction and solidification take place at a constant temperature, and systems in which the compound dissociates when heated to a certain temperature, and one of the dissociation products may be a liquid. In such cases solidification or liquefaction may take place through a considerable range of temperature.

# Methods for ascertaining the Constitution and Properties of Alloys.

There are many methods employed for studying the changes which occur during the passage of metals and metallic alloys from the liquid to the solid state, and for the determination of the constitution and properties of the solid mass.

The most important of the methods used in modern research are—

The thermal method.
Microscopical examination.
Mechanical testing.
Electrical and magnetic testing.
Chemical methods, both analytical and synthetical.

The Thermal Method.—This method of investigation has proved of immense value, and has led to many interesting and valuable additions to our knowledge of the mechanism of solidification and cooling. In taking a cooling curve, the platinum and platinum-rhodium or platinum-iridium junction of a thermo couple pyrometer, suitably protected by a fire-clay or porcelain sheath, is inserted in the mass of molten metal. The couple wires are connected by suitable leads to a deadbeat, high-resistance galvanometer of the D'Arsonval type, and the deflections of the mirror are read off on a suitable scale at regular intervals of time until the alloy has cooled. The temperature equivalents of the galvanometer readings are obtained from the calibration curve. This curve is obtained by noting the deflections of the galvanometer corresponding to a number of known temperatures, and plotting a curve having galvanometer deflections and temperature as co-ordinates. The temperatures corresponding to each interval of time are plotted as ordinates, and the corresponding time intervals as abscissæ, and in this way is obtained what is known as a "time-temperature" cooling or heating Instead of the time intervals elapsed since the beginning of the observations, there may be plotted as abscissæ the actual intervals of time required for a definite temperature fall, and in this case there is obtained what is known as an "inverse rate" curve.

A time temperature curve (see Fig. 1) may be regarded as the resultant of two movements at right angles to each other. If these are equal, the resultant is a straight line at forty-five degrees to the direction of motion.

If the temperature movement is irregular, the result is a curve, or several curves, or curves and straight lines. If the temperature remains steady, a straight line is obtained equal in length to the time the temperature is constant.

When a red-hot body—such, for instance, as a lump

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of copper or platinum—cooling in air is examined, the curve is at first steep, gradually becomes less so, and finally approaches a horizontal position as it cools (see Fig. 1, A). This is on account of the greater difference between the temperature of the metal and the surrounding medium when hot in comparison to the same metal when it is approaching the temperature of its environment.

If a pure molten metal is tested by this method—*i.e.*, antimony—the curve will at first descend sharply until the temperature drops to the freezing-point of antimony, but as soon as it is reached, solidification of

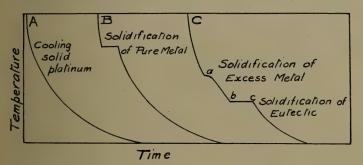


FIG. 1.—EXAMPLES OF COOLING CURVES.

the metal commences, with liberation of the latent heat of fusion, and the temperature remains constant until the whole of the metal has solidified. The result is a horizontal line equal in length to the time taken by the metal to solidify. When solidification is complete, the curve takes the same form as the red-hot copper or platinum (Fig. 1, B).

If, instead of pure antimony, an alloy of antimony and lead, containing more than 13 per cent. of the former, be examined, the cooling curve is very different. Antimony and lead belong to the class of alloys whose component metals are soluble in each other in the liquid state,

but entirely insoluble in the solid. These metals form an eutectic whose composition is antimony 13 per cent., lead 87 per cent., and which melts at 247° C. Pure antimony melts at 632° C., and pure lead at 327° C.

An alloy of equal parts of lead and antimony contains 42.5 per cent. free antimony, and 57.5 per cent. of the eutectic. In cooling this excess of antimony will solidify completely before the 57.5 per cent. of eutectic can begin to freeze; but the solvent power of the eutectic

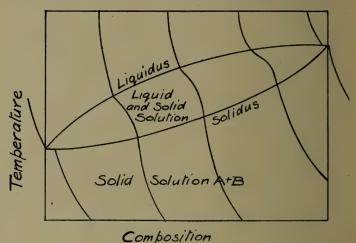
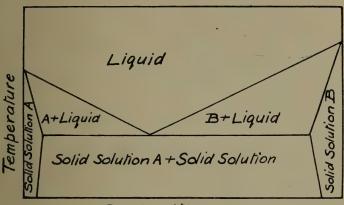


FIG. 2.—EQUILIBRIUM DIAGRAM OF ALLOYS WHOSE COMPONENT METALS ARE SOLUBLE IN EACH OTHER IN THE SOLID STATE.

for antimony prevents any of that metal crystallizing until the temperature has fallen considerably below 632° C. It is not until a temperature of about 409° C. is reached that solidification begins. The curve obtained shows that the first deviation from the normal curve of cooling solids is not abrupt, but is rounded, and that after the first arrest the curve does not return to the normal, as in the case of pure antimony after solidification—the reason being that at 409° C. only a por-



## Composition

Fig. 3.—Equilibrium Diagram of Alloys whose Component Metals remain Partially Soluble in each other in the Solid State.

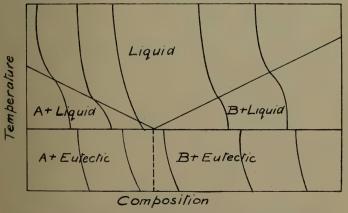


FIG. 4.—EQUILIBRIUM DIAGRAM OF ALLOYS WHOSE COMPONENT METALS ARE INSOLUBLE IN EACH OTHER IN THE SOLID STATE.

tion of the excess antimony solidifies, the remainder solidifying continuously over a considerable range of temperature, A-B (Fig. 1, C). When the whole of the excess antimony has fallen out of solution, the eutectic begins to freeze, and during its solidification the temperature remains constant, giving a horizontal line. When solidification is complete, the curve assumes the normal course.

In the investigation of a series of alloys, cooling curves are taken of a large number of mixtures of the two metals varying in composition from 100 per cent. of one metal to 100 per cent. of the other. The temperatures at which arrests take place are plotted as ordinates against composition as abscissæ, and lines are then drawn through the several records corresponding to the points of first, second, and subsequent arrests. way there is obtained what is known as the "diagram of thermal equilibrium," which shows the temperatures of beginning and completion of solidification of all alloys of the series, and also the eutectic point, and the composition and temperature of separation of chemical compounds. The line representing the commencement of solidification is known as the "liquidus," and that showing completion of solidification the "solidus." Typical diagrams for alloys, whose component metals are soluble, partially soluble, and insoluble in each other in the solid state are shown in Figs. 2, 3, and 4.

The Microscopic Method.—The systematic study of the structure of metals and alloys as revealed by the microscope has proved one of the most valuable aids in determining their constitution and the changes which they undergo when submitted to thermal and mechanical treatments.

Metals and alloys remain opaque even when reduced to very thin sections, such as are employed in the examination of rocks. It is therefore necessary to prepare a polished surface, and examine it by reflected light. The manner of preparation varies with the nature of

the metal or alloy. The first step is to obtain a representative section of suitable dimensions. In the case of metals which are comparatively soft, this may be effected by sawing and filing. In the case of hard, brittle materials, pieces may be chipped off or cut by a lapidary's wheel, and one face ground level on an emery or carburundum disc. The smooth, level surface of the specimen has next to be prepared for the final polishing, and this is usually done by rubbing on emery papers of increasing fineness, using first ordinary grades, and then French papers such as are used by steelengravers, numbered o to oooo. The rubbing may be done by hand, on strips of paper stretched on a hard wood or glass support, or it may be done mechanically by using a machine by means of which discs covered with the emery-papers are rapidly rotated and the specimen gently drawn across them. In the case of soft metals mechanical grinding is not permissible on account of the tendency of such materials to spread or flow. The grinding on each paper is continued with gradually diminishing pressure until all the scratches produced by the previous paper have been removed. The specimen is turned through 90 degrees from time to time, so that each set of new scratches are at rightangles to the previous ones. In this way it is easy to see when the coarser scratches have been removed. After the rubbing on the finest paper (No. 0000) no coarse scratches should be visible, and the specimen ready for final polishing. This may be effected on a rapidly rotating wheel covered with cloth or chamois leather, kept wet or dry, and upon which a quantity of polishingpowder is sprinkled. Wet polishing takes considerably longer than the dry, but is more satisfactory, and for specimens to be examined under very high powers is essential.

The polishing-powders employed are washed jeweller's rouge, diamantine powder, emery flour, alumina obtained from the calcination of ammonium alum, oxide

of iron from the calcination of oxalate of iron, magnesia, and others. Globe metal polish, spread on flannel or chamois leather, is also largely used for soft metals.

In some cases it is advisable to avoid the use of water, and to moisten the powder with paraffin oil. This is especially the case with copper and copper alloys.

In the case of very soft alloys it is almost impossible to obtain a good polish without deforming the surface, so that other means are employed, such as casting the molten alloy on to a smooth, polished surface like glass or mica, in contact with which it is allowed to solidify.

As the examination has to be made by reflected light, the illumination may be either oblique or vertical. The former is only possible with low powers, and the most convenient form of reflector is that known as the Sorby-Beck, which slips on to the objective. For vertical illumination and high-power work the reflector has to be placed behind the objective, and in this case is either a thin glass disc placed at 45 degrees to the opitcal axis, or a right-angled, total-reflecting prism.

A number of different types of microscope have been specially designed for the examination of metal surfaces, and these offer certain advantages over the ordinary form of stand, especially as regards provision for coarse focusing adjustment by raising or lowering the stage, instead of moving the tube. This is a special convenience when using an illuminator placed in the tube of the microscope, as its position is fixed, so that the beam of light once focussed into the illuminator remains so with objects of varying thickness and objectives of different working distances.

Any form of microscope can, however, be employed, especially if visual examination only is required; but where photographic records are required, a microscope specially designed for the purpose with wide body-tube is advisable.

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In examining the specimen it must be placed on the stage, so that the prepared surface is parallel to it and at right-angles to the optical axis of the microscope. A number of mechanical devices for holding the specimen so that the surface is level are employed by some workers, but these are not indispensable. The simplest method is to obtain a number of brass tubes of different lengths and diameters, with their ends cut perfectly true. The specimen is placed polished face downwards on a glass slide, a tube just large enough to pass over it is selected, a quantity of plasticine or soft wax is placed in the centre of another slide, and this is pressed into the tube until the slide is in contact with the brass ring.

The prepared specimen should present a uniform mirror-like surface unless the material contains constituents of different degrees of hardness. When an alloy containing constituents of different degrees of hardness is polished on a soft substance such as cloth or chamois leather, the softer portions wear away more rapidly, so that the harder substances are left in relief. The specimen should, therefore, always be examined under a moderate power without further treatment. In this way a great deal of valuable information can be obtained as to the relative hardness of the constituents, the presence of cracks, blowholes, oxide, slag, or other defects and inclusions in the metal.

As a rule further treatment is necessary in order to render visible the structure and to distinguish the constituents of the alloy. This further treatment is usually the corrosive action of some chemical reagent which attacks the micrographic constituents at different rates. The process of thus attacking the material is known as "etching."

The etching reagents which may be employed are somewhat numerous, and experience is necessary in order to decide which is the most suitable for any particular purpose. Those most frequently used are nitric,

hydrochloric, and picric acids, tincture of iodine, ammonia, ferric chloride, ammonium persulphate, and

copper ammonium chloride.

Nitric acid is largely used for iron and steel, coppersilver alloys, phosphor copper, and many others. It is preferably employed as a dilute solution in alcohol (I or 2 per cent.).

Hydrochloric acid is especially useful for alloys con-

taining much tin.

Picric acid is much used for steels, as in alcoholic solution its action is slow and uniform.

Ferric chloride is generally useful for bronze and

brass, and many other copper alloys.

Ammonium persulphate is also very useful for copper alloys.

Copper ammonium chloride has been extensively

employed for etching steels and copper.

Alloys containing much aluminium or zinc are best attacked by caustic soda.

Aqua regia is employed for alloys of platinum and

gold, usually at very near the boiling-point.

There are many other reagents in use for special purposes, but those mentioned are the most generally useful, and in special cases a suitable reagent is usually suggested by considering the chemical characteristics of the metal to be examined.

In addition to chemical methods of etching there is a method known as "heat-tinting." When heated in the air, many metals and alloys become coated with a thin adherent film of oxide, and showing the colours of thin films. Different metals and compounds oxidize at different rates, and Stead has made use of this fact in distinguishing between certain constituents of iron and steel. The method is also specially useful in the case of many copper alloys, particularly those containing silver or antimony.

The process is usually carried out by heating the specimen on a hot plate until the polished surface ALLOYS · 179

assumes a decided colour due to oxidation, and then cooling quickly by floating on mercury.

The examination of a specimen should be made in

three stages:

I. The polished but unetched surface.

2. After lightly etching to distinguish the constituents.

3. After deep etching in order to show the crystalline structure of the material.

It is somewhat difficult to decide exactly to what extent the etching should be allowed to proceed, so that it is better to first etch *very* slightly and examine under the microscope. The etching can be repeated until the structure is clearly developed.

The various constituents which may be found in alloys have already been enumerated, and it would be out of place to attempt a detailed description of their appearances in different alloys, under the various possible conditions of thermal, mechanical, and other treatments. A few general indications are given, but for a more comprehensive description of the structures of individual alloys, reference should be made to the various treatises on alloys and metallography.

If one portion of the material wears away more quickly in the polishing, it indicates the existence of at least two constituents of varying hardness. When in this way one or more constituent is left in relief by polishing or by etching, and the specimen is examined by oblique light, only the edges or sides of the portion in relief are illuminated, and the remainder appears dark. If there is no unevenness or irregularity of the surface, none of the incident rays are reflected into the tube of the microscope, and consequently the whole surface appears dark.

In some cases the specimen is unequally darkened or attacked by the etching reagent, or assumes colour tints more rapidly in some parts on heating in air; this is evidence of a variation in the constitution of the alloy. There are, however, some exceptions to this, such, for

instance, in the case of alloys containing a constituent relatively more electro-positive than the others, so that an electrolytic action is set up between them. If a heat-tinted or etched sample exhibits a graduated colouring or corroded appearance, it is almost certain that the alloy contains a non-homogeneous solid solution of one constituent in another. Irregular solid solutions are frequently found in the alloys of copper with silver, or antimony or tin, etc.

Eutectiferous alloys, especially if the eutectic is present in considerable quantity, usually show, either with or without etching, an iridescent colouring somewhat like mother-of-pearl. Although it is very strong, an iridescent colouring is not absolute evidence of the presence of an eutectic, because in some cases the crystallites of which metals are built up may on strong etching be irregularly attacked, so that alternate edges are left more or less in relief. This causes a chromatic appearance due to an interference of light. Homogeneous metals never yield iridescent tints, but eutectics invariably do so.

Eutectics may be of various forms, such as, for

instance:

I. The rectiplanal, in which the two phases have separated during solidification in separate flat plates. The lead silver eutectic has this form.

2. The cellular, in which plane plates of one constituent are disposed in a radiating manner, the second constituent filling up the interstices. The lead antimony eutectic is of this form.

3. The curviplanal, in which the constituents occur in the form of curved plates. This form is seen in silver and copper alloys, and in some steels. In some very slowly cooled alloys the eutectic assumes a crystalline geometrical form. The triple alloy of lead, antimony, and tin exhibits very perfect geometric forms. The gold and lead eutectic assumes a cubical form if slowly cooled, and spherulitic if quickly cooled.

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4. A branched form, such as in the lead-tin eutectic. Reference has already been made to non-metallic mechanical enclosures, which are frequently present in alloys.

Wrought-iron always contains masses of silicate slag or cinder elongated in the direction of rolling. Steel also frequently contains slag or sulphide of manganese,

the latter showing a dove-grey colour.

Copper-tin alloys sometimes contain stannic oxide in well-defined crystalline shapes. The detection of slag and other occluded substances in metals is a matter of considerable importance, as they tend to influence adversely the mechanical properties of the material, and may form centres of weakness from which fracture

ultimately results.

The microscope has lent invaluable aid in determining the nature of the changes in structure and constitution brought about by thermal or mechanical treatment of metals and alloys. It has shown that there is a very marked connection between structure and the physical and mechanical properties of the material, and has been the means of indicating the nature of the treatment to which a particular material should be submitted in order to render it suitable for a specific purpose. It is possible from a careful microscopic examination to read the whole life-history of the metal as regards its thermal and mechanical treatment.

The microscope has proved specially useful in the investigation of failures, not only as regards detecting the cause, but also as indicating means for preventing a recurrence of similar accidents.

Electrical Methods.—It has long been recognized that the specific electrical resistance, or its reciprocal, the specific conductivity, is very closely connected with the constitution of an alloy. It has been experimentally shown that in no series of alloys is the conductivity greater than that of the component metals. The conductivity of alloys gives a certain amount of definite information as to the nature of the alloy.

Alloys whose component metals are insoluble, or very nearly so, in the solid condition, have a conductivity which is a linear function of the composition. A curve having as co-ordinates, specific conductivity and volume concentration is a straight line. In the case of alloys whose components are soluble in the solid state, the curve connecting conductivity and composition is a smooth **U**-shape.

The alloys of metals which are only partially soluble in each other in the solid state, and which form an eutectic, show a rapidly diminishing conductivity at the ends and a straight line relationship in the centre. The curve is a combination of the straight line, and the **U**-shaped curves shown by the insoluble and soluble

groups of metals.

In the case of those series of alloys in which chemical compounds are formed, it is found that the compounds conduct like pure metals, but that their conductivity is lower than that of the better conducting metal. The curves connecting conductivity and composition show maxima or minima points. A sharp kink in the curve with the point upwards indicates that the compound present is able to form a solid solution; whilst if the curve consists simply of two intersecting straight lines, it indicates the presence of a compound which does not form a solid solution.

Mechanical Methods.—As is well known, metals vary greatly as regards their strength, ductility, and elasticity, and remarkable changes are produced by alloying with varying proportions of another metal. The complete examination of a metal or alloy includes the determination of compressive and tensile properties, but, on account of the extensiveness of the subject, it is impossible to deal with it here, and reference must be made to standard works on the strength and general properties of alloys. The hardness (mineralogical) of a metal is very greatly altered by the addition of another metal, and the manner in which the hardness changes

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depends upon the type of alloy produced. It is found that, as in the case of fusibility and conductivity, the hardness bears a distinct relationship to the conditions of solubility of the component metals after solidification.

The hardness is a linear function of the composition in the case of two metals which are insoluble in each other in the solid state.

In the case of metals remaining mutually soluble in each other in the solid state, the hardness relation to composition is shown as a smooth curve having a distinct maximum at about 50 per cent. of each component. The hardness at this point is usually about double that of either of the component metals.

If the metals are partially soluble in the solid, the hardness relation is shown by two smooth curves joined by a straight line. In the case of metals forming compounds, the curve shows a maximum at the composition at which the compound is formed, if it is also capable of forming a solid solution. If a single compound be formed in the absence of solid solutions, the relation of hardness to composition is represented by a simple diagram formed by the intersection of two straight lines, the intersection corresponding to the composition of the compound.

Other Methods of Examination.—A great many other physical properties of alloys have been studied in relation to the constitution, and in some cases information has been obtained which has been valuable in supplementing the evidence obtained from thermal and microscopical methods. In other cases the information obtained must be considered somewhat unreliable until further investigation has been made.

The density of alloys shows, under certain conditions, variations which bear a relationship to the constitution. It is, however, more usual to use the reciprocal of the density—the specific volume.

The specific volume concentration curve for alloys

of metals insoluble in each other in the solid state is

a straight line.

The alloys of metals forming solid solutions show too small a variation in volume to be of any use, for a solid solution is usually formed without change of volume, and specific volume curves are useless in distinguishing between solid solutions and conglomerates.

In the case of metals forming compounds the alloys show at certain compositions marked variations in specific volume. It does not, however, follow that a distinct break in the curve occurs exactly at the composition of the compound if solid solutions are not formed. There is no general rule as to the direction of the change, as sometimes compounds are formed with a considerable expansion, and in other cases a contraction in volume results from the combination.

The thermal expansibility, electro-motive force, changes in magnetic properties, and thermo-electric power, have all been useful in certain cases, but much further investigation is necessary before any general laws expressing relationships between them and the constitution of an alloy can be formulated.

The chemical methods of examination of alloys, and of residues left after treating an alloy with a reagent, are of much importance. There are, however, especially as regards the latter, many difficulties to be overcome, and the results require cautious considerations. The subject is too wide to be intelligently dealt with in the space available, but information may be obtained from many textbooks on metallurgical chemistry.

#### CHAPTER XVIII

### DENTAL AMALGAMS

Properties.—There is probably no subject of dental interest which has evoked greater interest and lead to such profuse literature as that of dental amalgamsfrom the writings of the trained metallurgist to that of the private practitioner, each putting forward his views and results with an assurance of finality, and so widely different from each other that the student of the subject is liable to be confused. Modern metallurgy, assisted as it has been with the rapid advance of our knowledge of the constitution of alloys, their chemical combinations, microscopic structure, melting-points, has assisted the dental profession in weeding out much that is useless in gaining a comparatively accurate basis to go upon. In what follows the attempt has been made to present the subject as it is, and to avoid every view that would lead to confusion, or the acceptance of theories which have still to be demonstrated.

Amalgams for dental purposes are generally confined—to those suitable for inserting as fillings, and should consist of alloys that are complete combinations with, or solutions in, mercury, of metals or alloys of other metals. That is to say, that after the finely divided alloy has been impregnated with the proper quantity of mercury, the resulting amalgam should disclose no metal or metals left unattached, and merely held in the amalgam by molecular attraction. As originally employed, amalgams consisted of filings of silver coins,

or powdered copper mixed to a paste with mercury and inserted into the cavity, and many years passed before amalgams as a class outlived the evils generated from these primitive fillings. It is only within comparatively recent years that the uses of amalgams have been fully recognized and appreciated, and their proper sphere mapped out and limited. It will be admitted, for instance, that gold as an all-round filling material still holds the premier position. It does not oxidize or stain the tooth, does not change in its relation to the cavity through volume changes, and, provided that it has been inserted properly in a well-prepared cavity, gives permanent results as far as it as a metal is concerned. Where the operator recognizes that the cavity is one into which any material can be inserted with accuracy, then that cavity should be filled with gold if permanency is desired.

Amalgams are generally limited to restorations in deciduous teeth, especially in the molar regions; to cavities in permanent teeth not readily accessible; where the insertion of gold would incur too severe a strain on the patient; where the tooth is too frail to withstand the malleting or hand pressure necessary for gold; where the difficulties attending the keeping of the cavity perfectly dry are too great; and where an impression for an inlay cannot be obtained for any reason. As a class, they may be considered to possess the

following properties:

I. They are readily inserted, being more or less plastic, and on this account can be made to fit closely to the cavity walls.

2. They possess good edge strength, being hard, not liable to fracture, and extensive contours can be safely built with them to replace lost tooth structure.

3. They resist attrition, are not soluble in saliva, and, with the probable exception of Sullivan amalgam, do not stain the tooth.

4. They do not readily oxidize in the mouth, the oxidation when present being entirely superficial.

5. By forming a watertight and insoluble plug, they

preserve the cavity against decay.

An ideal amalgam, on the other hand, should possess

the following properties:

- 1. It should be readily inserted with accuracy, and not tend towards friability when burnishing pressure is applied.
- 2. It should be insoluble in saliva, and should not favour the formation of any salt injurious to the tooth structure or health of the patient.

3. It should harden moderately fast, and thus lessen

the chances of change of shape.

- 4. When hard, it should be unalterable in shape, presenting neither expansion nor contraction, and not liable to change of shape when subjected to the force of mastication.
- 5. It should continue to possess good colour, and not oxidize in the mouth.
- 6. It should not act as an irritant to the pulp when inserted within reasonable distance of that structure, either by electrical or thermal conductivity, or by reason of the properties of the metals contained in it.

7. It should not stain the tooth structure, and when polished, its colour should not render it conspicuous in

relation to the rest of the tooth.

8. It should amalgamate freely and thoroughly, and should possess a definite combining weight with mercury.

9. It should not induce electro-chemical action be-

tween the different metals in the mouth.

No amalgam at the present time possesses all these properties. For some time the endeavour has been to produce an amalgam which would disclose a slight expansion after setting, the hope being that the expansion would bring the amalgam into closer contact with the cavity walls, and so reduce the chances of ingress of bacteria. Examination of many amalgams

prove that they do expand when inserted into a thin glass tube. The tubes either cracked or broke asunder, due to the expansion of their contents; or, inserted into a Wedelstaedt ring and polished, the expansion was evidenced by the fact that the plug, once removed from the ring, could not be replaced. If expansion occurred in the direction of the cavity walls and in the line desired by the operator, and that to a very slight extent, all might be well. In large contours restored by amalgams, in many instances the expansion after several months or a few years seems to be from a common centre, the result being that the cavity edges are left unprotected, even although the filling has drawn attention to the expansion which has taken place by impinging on the bite if exposed on a grinding surface

What the profession is seeking is an amalgam which neither expands nor contracts, but remains exactly as the operator left it when polished free of scratches and well burnished. Expansion of an accurately inserted filling is unnecessary; and even although the expansion were to take place in the line desired, many teeth would be too frail to withstand the pressure exerted on the cavity walls. Contraction even in a modified degree should condemn an amalgam for dental purposes.

The metals in amalgams, with the exception of the amalgam of finely divided copper and mercury already referred to in the chapters on copper and mercury, and known as "copper or Sullivan amalgam," are present as alloys, the mercury being added to the alloy, which is either in the form of medium fine filings or shavings. As separate metals they all exhibit some property when amalgamated, which prohibits their use in this form.

Gold added to mercury amalgamates well, being soluble in an excess of mercury, but does not harden sufficiently, and does not possess sufficient edge strength, besides contracting excessively.

Platinum requires an excess of mercury to render the

amalgam plastic, does not harden well, lacks edge

strength, and contracts.

Silver amalgamates well, the union of the metals being accompanied by evolution of heat; but fillings of this amalgam expand excessively, and discolour—the tooth through oxidation.

Tin amalgamates readily, but never hardens suffi-

ciently.

Copper, if finely divided and freshly deposited, amalgamates with mercury, but much less rapidly than gold, silver, or tin. (See Copper Amalgam.)

Palladium amalgamates readily, becomes fairly plastic, the union of the metals being accompanied by a rise in temperature. The amalgam, however, discolours, and the prohibitive price of palladium, due to its scarcity, has led to its disuse.

Although the separate metals exhibit these properties when amalgamated with mercury, they also produce certain definite effects if added as constituents of alloys.

Thus:-

Gold improves the working qualities of an amalgam, renders it more plastic, slows the time of setting, improves the edge strength, counteracts shrinkage, and improves the colour by counteracting oxidation, but increases the flow if in excess.

Platinum counteracts oxidation, hastens the setting, increases the edge strength, overcomes the tendency to change of form after setting, but increases the amount of mercury required.

Silver increases the edge strength and rigidity, counteracts contraction, and reduces the amount of mercury required. This metal, however, increases oxidation.

Tin amalgamates freely, rendering the amalgam more plastic, reduces conductivity, but exerts a contracting effect, besides counteracting the expansion produced by the addition of silver.

Zinc is employed to replace platinum, and requires less mercury to render the amalgam plastic. The metal

whitens the amalgam, hastens setting, and, by some authorities, modifies expansion and contraction. The view at present is generally accepted that zinc, when present, causes constant changes to occur in the amalgam, such as increasing the flow, and by reason of its galvanic properties causes disturbances in other amalgams, and is reduced in volume itself. This reduction in volume is attributed to the loose form in which zinc combines with the other metals present, and the presence of oxidized zinc in the soluble form, which in time is washed out.

Copper increases the edge strength, counteracts contraction, hastens the setting under water, and by some authorities is held to exert its therapeutic action on the tooth by depositing the antiseptic copper salts in the dentinal tubules.

Against this view it can be stated that several teeth showing the blue-black stain attributed to copper have been tested and no copper found, while the advocates of copper give instances where arrested decay has been discovered impregnated deeply with copper stain. It is now generally accepted that staining beneath the free margin of an amalgam filling, besides being undesirable, is due to the ingress of food débris and moisture, and should be traced to contraction or change in the filling and not to an inherent protecting virtue in the amalgam.

The Composition of Modern Amalgams.—These are the effects produced on an amalgam by the addition of the separate metals, and must be accepted in the broadest sense, as a varying proportion of the same metal will produce different results. Dr. Foster Flagg was about the earliest researcher in the subject of dental amalgams to test and formulate with comparative accuracy these effects, making use, for instance, of the metal zinc for its whitening properties in his "facing alloy," and containing 3 parts zinc, as will be seen from the list given. In his "contour alloy" he takes advantage of the improvement in the colour, and the reduced oxida-

tion of the surface by the addition of 5 parts gold. In his "submarine alloy," intended to be restricted to cavities extending under the free margin of the gum, and where it is impossible to keep the cavity perfectly dry, copper 5 parts are added, as he found that this metal hastened the setting, and also facilitated the crystallization of the amalgam when wet with saliva.

Besides Dr. Flagg, the profession has had the advantage of the experience of such eminent men as Kirk, Black, Bain, Knight, Burchard, Fletcher, Fenchel, and many others, all working on the same problem of how to produce an alloy which will not expand, contract, flow under pressure, which will not discolour, injure the pulp, and when reduced to powder or shavings and amalgamated with mercury, will harden in a reasonable time.

From the earliest researches we find the two metals silver and tin predominating in the alloys. Silver and tin, when melted together, can be balanced in such proportions that the expansion of the silver can be regulated to overcome the contraction produced by tin. The two metals also possess several eutectics, freely intermingling, and closely approximating to a chemical union. Experience proved that such an alloy when amalgamated was lacking in edge strength, resistance to flow, etc., and the efforts were then directed to observe the effects produced by the addition of other metals to improve the known defects of the silver-tin amalgams. Dr. Kirk, in Litch's "American System of Dentistry" (p. 796, 1887 edition), was about the earliest to direct attention to the possibilities of building up an alloy, taking advantage of the quantivalence and chemism of alloys, in which we find that chemical compounds contain the elements in fixed proportions, these being always simple multiples of their atomic weights. Carried into practice, this consists in melting the metals, allowing the liquid to partly cool slowly, and by pouring off the still liquid portion, the crystallized metals which have combined are found on analysis to be united in their equivalent atomic ratios.

Such an alloy containing silver, tin, and copper, gives the proportions, silver 65, tin 30, copper 5, with a formula of Ag SnCu. The alloy is dark grey in colour, harsh to work when reduced to medium grit by filing, sets moderately fast, possesses good edge strength, and, from the writer's experience of it, behaves very well; but a sufficient period of time has not elapsed to test it for contraction, expansion, or flow, when in the mouth. Dr. Black, in his book on "Operative Dentistry," gives the results of his experiments, beginning with silver-tin solutions, and making tests as to the effects of the addition of such metals as gold, copper, platinum, zinc, etc., these additions being in the nature of balancing metals added to increase the edge strength. and to withstand the pressure exerted on a tooth during mastication; also to overcome expansion, contraction, and flow. His results led him to declare that "no advantage whatever is derived from adding gold or platinum to alloys, but as long as these are used very sparingly they do not do much harm. Copper, not more than 5 per cent., if alloyed with silver before combining with the tin, so as to insure a perfect alloy, increases the strength of the amalgam without doing injury in other ways, and seems desirable. In my present view it is the only modifying metal thus far known that is desirable."

Much has been written since Dr. Kirk, and later Dr. Black, have put their ideas before the profession, Dr. Black's work receiving severe criticism from Dr. Fenchel, who denominated Dr. Black's measurements as superficial, and his metallurgical investigations as barren of a true comprehension of the internal structure and chemical constitution of alloys. There certainly existed fair grounds for Dr. Fenchel's criticism as to the disregard paid by Dr. Black to the internal structure and chemical constitution of his alloys, but so far as

investigations have gone in this branch of dental research, it has not been conclusively demonstrated that an alloy possessing no defects from the chemical point of view has ever proved ideal when amalgamated and inserted in the cavity and exposed to varying salivas, strains during mastication, and in varying depths of cavities.

Operators of experience know that alloys are prepared for the profession containing gold and platinum,

Name of Alloy.		Silver.	Tin.	Copper.	Zinc.	Gold.	Plati- num.
Ash and Sons	. *	66.54	27.16	5.02	0.9		
Davis'	.*	42°4I	51.42	3.21	_	3.2	
Fellowship				3.18	1.19		
Flagg's contour alloy .		58.00	37.00			5.00	
Flagg's submarine alloy	у	60.00	35.00	5.00			
Flagg's facing alloy .	. *.	37.00	35.00		3.00	5.00	
Fletcher's platinum an		- '	-				ĺ
gold alloy		43°35	50.35	1.65		3.35	1.30
Globe,	*	44.89	51.90		0.50		
Justi's Superior .	. *	35.20	69.10			0.32	0.80
Lawrence's		44.06	50.43	5.21			
Standard dental allo			- 10				
		52.00	40.60	3.00	!	4.40	
True Dentalloy	.*	65.91	27.13	5.21			
		46.00				1.70	
Twentieth Century .		67.03		4.87	1.10	<u> </u>	

besides silver, tin, and copper, which have satisfied them in all essential points, and are giving good results after being several years in use; not in isolated cases, but in sufficient numbers to induce them to employ the same alloy year after year.

Alloys as employed in industry and the arts are not compounded in proportions to form chemical solutions, but to produce definite physical results, such as the alloying of gold to reduce carat increases the hardness, in which example the copper and silver are simply held

<sup>\*</sup> Definite parts by weight; the others are expressed in percentages.

EXHIBIT OF MODIFIED SILVER-TIN ALLOYS.

Crushing Stress.	290 335 329 380 380 330 330 300–373 200–373 200–343 416–450 200–290 200–200 20
Flow.	3.67 3.67 5.05 6.05
Expan- sion.	10 40 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
Shrinkage	000000000000000000000000000000000000000
Percentage of Mercury.	33.33 33.33 33.33 33.33 33.52 33.53 33.53 40.65 40.65 40.65 44.12 44.12 44.12 44.12 46.98 35.00 46.98
How Prepared.	Fresh-cut Annealed
i	44 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4
Silver.	65.00 66.75 66.75 66.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75 61.75
Formula (Modifying Metals).	None None None None None Cold 5 Platinum 5 Platinum 5 Copper 5 Copper 5 Zinc 5 Zinc 5 Zinc 5 Zinc 5 Bismuth 5 Cadmium 5 Lead 5 Aluminium faluminium i Aluminium i Aluminium i Aluminium i Aluminium i

in a gold matrix, especially in the lower carats; the several grades of dental alloy, bronzes, brass, etc., being other examples. The set of formulæ given on p. 193 and the table on p. 194 from Dr. Black's book on "Operative Dentistry," will give an idea of the wide variations existing between many of these alloys.

The necessity for reducing the alloy to filings or shavings, and also the amalgamating with mercury, is sufficient in the writer's opinion to prevent dogmatism, in the present state of our knowledge, from being applied

to this much-vexed question.

Preparation of Alloys.—The metals entering into an alloy to be afterwards mixed with mercury should be prepared from chemically pure metals, and the mercury employed should be electrically pure, as small traces of impurities are capable of exerting undesirable effects. In Britain, theoretically pure metals are easily obtained from reliable bullion merchants, silver, for example, being obtainable 999 6 parts pure per thousand. In preparing the metals for melting they are improved by being washed in a solution of caustic soda, and the soda removed by water or absolute alcohol. The actual melting may be effected in several ways, either by using an electric vacuum crucible where air is withdrawn; by an ordinary electric crucible using charcoal chips, or passing in hydrogen gas during the melting-stage of the more oxidizable metals to reduce loss through oxidation; or by an injector furnace, such as Fletcher's, Russell's, using a salamander or a fine fire-clay crucible, covering the metals with charcoal and closing the crucible with a tight-fitting cover. In using the electric vacuum crucible, a pyrometer with a porcelain-covered thermocouple of platinum, and platinum alloyed with 10 per cent. rhodium, affords an accurate means of denoting when the several metals are dissolved. The type supplied with the crucible of pure carbon, or of fine fire-clay and separate from the heating element, is best, as results are much improved if a new crucible is employed for each

melting. The same may be said of the ordinary electric crucible as made by Messrs. Mitchell and Company, and supplied by Messrs. C. Ash and Sons, Ltd. The type of furnace prepared with the heating element embedded in the walls of the crucible is open to the objection that cracking of the crucible entails rewiring and loss of time, and a new detachable crucible is recommended for each melting on account of the metallic oxides left adhering to the crucible after a melting, and which would affect any subsequent melting, by increasing the possibility of absorption of the oxides by the alloy.

In all cases the crucible, whether of the carbon. graphite (salamander), or fine fire-clay variety, should be well annealed by being raised to a bright red heat, and allowed to cool slowly in the inverted position. This test will expose any fault in the manufacture, whether in the form of cracks or excessive brittleness. It is then coated on the inside with powdered charcoal, or rubbed with a rod of carbon until the surfaces are well covered. as this tends to reduce oxidation of the metals, lessens the chances of the metals passing into the body of the crucible by absorption, and enables the molten metal to run freely. The metals to be included in the alloy, having been carefully weighed and checked, are ready for the melting process. In alloys containing gold, copper, silver, and tin, the order of melting may be varied. Some authorities contend that in melting noble metals, the melting-point of the highest should be reached so as to insure complete solution of the metal. In practical goldsmith work it is the rule when melting gold, silver, and copper, to melt the gold and copper together with one-half silver, and when molten to stir in the remainder of the silver. The gold in such cases is either in the granulated form or rolled into thin cornets to insure rapid solution. In practical alloy making such as is now under consideration, this method proves satisfactory when employing the ordinary electric furnace and crucible or the injector furnace. Where the vacuum crucible is in use a thermo-couple of the detachable variety is employed, and the temperature necessary for bringing the metals to solution obtained from previous experience. A slight reduction in the temperatures necessary is allowed in melting *in vacuo*, compared with

those exposed to ordinary atmosphere.

A little borax and powdered charcoal is added to the crucible charge, and the temperature raised until the action of the borax ceases and the metals dissolve. Stirring with a carbon rod insures thorough mixing. If tin or zinc are to be added, a little more charcoal is added, meanwhile cutting off the heat to the extent of keeping the charge molten and no more. The moment the tin or zinc is to be added the heat is entirely cut off, and the addition of tin or zinc made either in small quantities or the entire quantity at once; the crucible contents are rapidly stirred, the crucible withdrawn, and the liquid alloy decanted rapidly into a clean and welloiled steel ingot mould. The mould is then rapidly chilled to fix the metals in their alloyed position, and to prevent the formation of several eutectics with the most of the tin confined to the surface of the ingot. The addition of the carbon tends to reduce the loss of tin or zinc through oxidation, and also to prevent as far as possible occlusion or absorption of oxygen from the atmosphere by the silver. Some authorities advocate the addition of a little common salt or ammonium chloride as well for the same purpose, but such an addition increases the fluid slag which is troublesome, when there is the powdered charcoal over and above to be contended with at the pouring stage.

The ingot of alloy should be weighed carefully to find the extent of loss through oxidation. From frequent experiments the loss through this cause can be brought down as low as 0.003 per cent. of the total weight of the alloy. By deliberately adding this quantity of tin or zinc to the original quantity required, the loss is allowed for, and the ingot should be nearly the weight of the metals previous to melting. Beyond 0.007 per cent. it is almost advisable to remelt and make the necessary addition, as the properties of the alloy are affected at and beyond this percentage of loss. By careful melting the loss should be limited to these two readily oxidized metals, tin and zinc, and occurs almost entirely at the first addition through too high a temperature and unnecessary exposure of the metals to the atmosphere when in the molten condition. By bringing a stream of hydrogen gas to play upon the liquid metals, this loss is said to be much reduced. By the vacuum process carefully worked out, and by charging all the metals into the crucible at once in layers arranged with the gold at the bottom, and the copper, silver, tin, or zinc in order, loss is said to be still further reduced. The ingot of metal is then reduced to shavings in a cutting machine, or placed in the jaws of a clean vice, with the ingot protected from the steel with washleather or several layers of tissue-paper, it is reduced to filings, using a medium coarse file. The filings are sifted to remove chips and insure uniform fineness, well screened with a magnet to remove file grit, and are ready for bottling. Filings at the present time most in favour, such as the silver, tin, and copper alloys, are harder to cut than the filings of silver, tin, copper, and gold alloys; and shavings of the alloy are extremely friable and do not amalgamate so readily as the medium filings.

Ageing of Alloys.—The term "ageing" as applied to the peculiar changes which occur in alloys in shavings or powdered form, after they have been prepared and set aside for some time, or have received special treatment to produce these changes artificially, are at the present time not fully understood. An alloy freshly prepared and amalgamated requires more mercury to render it plastic; it also sets more rapidly, and its physical properties are materially affected compared with an alloy which has been "aged," either by keeping it for some months before using or by subjecting it to

one of the "ageing" processes to be described. The only advantage gained by "ageing" an alloy artificially is that the effects can be attained almost at once and the amalgam tested for its physical properties. An alloy which has been prepared and kept in stock for several months without artificial "ageing" while being much more plastic than one freshly prepared, is slower in setting, and generally contracts on setting compared

with tests made from it when freshly cut.

Several theories have been advanced to explain the changes produced by "ageing." Oxidation was held accountable; but the evidence in support of this view is entirely lacking, as alloys are generally kept sealed from the date of their preparation, and microscopic examination has failed to disclose darkening or any other change generally associated with oxidation. Relief of strain produced by the cutting or filing of the alloy is also receiving serious consideration at the present time, and alloys are generally held to be improved in their physical properties if they are sealed hermetically in well-tempered glass bottles and heated to 100° C. for one hour. All efforts so far have failed to produce "ageing" by any process entailing a reduction of temperature such as immersion in cold water, or surrounding the vessel containing the alloy with ice. Dr. Black and others have stated that little importance need be attached to the process of "ageing," and lately several noted alloy manufacturers have emphasized the importance of not using alloys that have been prepared or kept in stock more than a few months.

The means adopted by several manufacturers to

produce "ageing" consist, or consisted, of-

I. Immersing the cut alloy in boiling water, either enclosed in sealed tubes or exposed to the water.

2. By exposing the cut alloy to the sun and shaking at frequent intervals.

3. By cutting or filing the alloy at a speed sufficient to generate heat.

4. By passing pure hydrogen, nitrogen, or oxygen gas into the vessels containing the cut alloy.

Testing Amalgams for their Physical Properties.—Amalgams are generally tested for their properties of expansion, contraction, and flow, most writers agreeing that every ingot of alloy should be carried through the tests, as no two ingots prepared from the same formula at different meltings will yield the same results. The methods adopted at present may be summarized as follows:

Expansion or Contraction.—By the Glass Tube Method: This consists in mixing the alloy with sufficient mercury to cause the filings or shavings to cohere, the amalgam being ready for use when squeezing in chamois leather fails to remove any excess mercury, and when the amalgam pressed firmly between forefinger and thumb receives the skin markings from the fingers. The quantity of mercury varies with the several alloys. is regarded as better practice to amalgamate the alloy in an agate mortar, using an agate pestel and adding the mercury drop by drop until the amalgam is coherent, and not soft and pasty. Or, by placing the alloy in a glass mixing tube, and adding the mercury drop by drop and shaking, the alloy absorbs the mercury and gradually becomes coherent. By removing the amalgam from the mortar or mixing tube and placing it in a small sheet of rubber dam previously washed with absolute alcohol to insure sterility, it may be worked up with the fingers, keeping the amalgam in the rubber dam as in a sack and free from contact with the fingers. The warmth of the fingers increases the plasticity of the amalgam. If excess of mercury is present, a little of the powdered alloy should be added in preference to expressing the surplus mercury, as the mercury may carry off traces of the gold, silver, and possibly tin. The practice of amalgamating the alloy in the palm of the hand should be discarded, as the operator runs the risk of absorption of mercury through the skin, with its

consequent effects; the amalgam becomes impregnated with bacteria from the operator's hands, and reduces considerably the value of present-day aseptic cavity toilet.

The prepared amalgam is packed with firm pressure into a thin glass tube (a small sized test-tube blown thin), and, making sure that there are no air spaces in the amalgam, the tube and its contents are set aside. Marked expansion will be followed by the cracking of the tube; contraction by the amalgam becoming loose in the tube if disturbed. Picrocarmine solution is employed to denote moderate contraction, the tube of amalgam being immersed in the solution, when the dye will infiltrate into any spaces present due to contraction. The tests have to extend over several days at least, as the amalgam continues to change during this period, as will be noted from Dr. Black's record of his experiments.

The Wedelstaedt Tube Method: This tube is about 3 inch in depth, and the same in breadth across the broadest part, tapering slightly. Is prepared of steel, about 1 inch in thickness, having the surfaces, edges, and bore turned accurately and buffed. The most useful type has a longitudinal groove cut on one side of the bore, and of the same depth and breadth from top to bottom. The amalgam is prepared and packed firmly to place in the tube, care being taken to fill the groove, as this prevents change of position of the hardened amalgam. The filling of the tube should be carried slightly beyond the surface, so as to insure an accurate levelling of the amalgam with the edge of the tube. After the lapse of forty-eight hours the surfaces of the amalgam are levelled with the margins of the tube by rubbing down on emery-paper, coarse at first, and latterly the finest flour emery, using a side to side and rotary movement to remove all scratches. The surfaces are then etched with dilute nitric acid to clean them, and also prepare them for microscopic

examination. The amalgam is gently tapped from the tube, and allowed to stand aside for a few days, placed into position in the tube, and any change noted. Expansion will be exhibited by the failure of the amalgam to go perfectly to place, any alteration being seen by employing an ordinary power laboratory microscope. Contraction will be exhibited by the amalgam remaining loose in the tube, and by studying the width of space between the amalgam and the tube at the prepared edges, the degree of contraction can be estimated. The high powered metallurgical microscope, with its condensing apparatus for illuminating metal surfaces, is employed to observe the distribution of the mercury through the amalgam, and also the distribution of the metals in the alloy before being reduced to filings and

amalgamated.

The micrometer has also been employed for registering expansion and contraction. The Wedelstaedt tube containing the set amalgam is placed in the micrometer and firmly secured. By bringing a delicate pointer to bear lightly on the amalgam surface, any change either in the direction of expansion or contraction is indicated by the pointer rising or lowering, and the degree of change is indicated in 1/20000 inch on a dial scale adjusted to the instrument. Dr. Black, who was about the first to employ the dilatometer altered and scaled down to 1/20000 inch, contended that to preserve a tooth, an amalgam filling should undergo an increase corresponding to an advance of at least 1/20000 inch in the altitude of a column 0.38 inch in height and 0.33 inch in diameter. This he termed a "½-point expansion," a "point" on his micrometer thus being equal to O.OOOT inch.

Edge Strength.—He also stated that a filling to withstand any crushing strain that might be exerted upon it during mastication should on a cube of 0.085 inch be capable of withstanding a pressure of 350 pounds, and not yield more than 0.002 inch. The dynamometer as now employed to test edge strength consists in a machine with a receptacle, into which the Wedelstaedt tube filled with the hardened amalgam is placed. A point is brought to bear on the amalgam surface, and by means of a screwed rod, pressure is brought to bear until the amalgam is found to yield. The pressure necessary to produce the yield is recorded upon a dial scaled on the same plan as crushing testing machines for alloys.

Flow of Amalgams.—By flow is meant the extent which an amalgam will yield or flow before a constant or intermittent pressure, such as is exerted upon fillings situated upon the grinding surface of a tooth during mastication. The test may be carried out on the amalgam in or withdrawn from the testing-tube. A constant pressure or a hammering stroke is brought to bear upon the amalgam, and the extent of the flow or change of shape, together with the strain necessary to produce

the change, are examined and noted.

These tests are admittedly different from those to which a filling is exposed in the mouth, such as the various degrees of acidity and alkalinity of saliva; the various breadths and depths of cavities; the various positions of cavities, whether exposed or not to the force of mastication; the varying pressure exerted during mastication; the habits of the patient, whether cleanly or otherwise; the varying foodstuffs, whether taken habitually sloppy or hard and fibrous; the various metals present in the same mouth. As theoretical tests, they afford a reliable means of testing an amalgam for its theoretical properties, but the personal equation of the operator must never be forgotten; whether he is painstaking and prepares cavities to suit the needs of an amalgam; whether he exercises care and judgment in bringing the powdered alloy and mercury together in proper proportion, and whether he inserts it with as much care as he would a gold filling in the same position.

#### CHAPTER XIX

# HARDENING, ANNEALING, AND TEMPERING OF METALS

THE subject has already been briefly referred to in dealing with steel and gold.

Hardening.—There seems to exist a certain amount of confusion regarding the application of the terms "hardening," annealing," and "tempering." The term hardening is more properly confined to the change effected in a metal by sudden cooling after it has been raised to a bright red heat or higher temperature. With steel, for instance, the sudden cooling of a finely constructed scaler or chisel will cause the instrument to snap off short if strain be applied; whereas, on undergoing tempering, the metal is found to possess greater elasticity and strength than before, and yet retains the fine cutting edge it may have received, even when employed to cut such hard substances as salivary calculi and enamel. In the case of gold-hardening, the metal can be affected by simply rolling or hammering. Advantage is taken of this in the manufacture of finger rings made to receive precious stones, where elegance and lightness are desired. The gold is hammered after being rolled, this bringing the molecules of the gold into more intimate contact, and to a greater state of tension, with the result that the gold is reduced in bulk but possesses greater rigidity and strength. The same change occurs in striking up a gold plate, the hammering with the horn mallet gradually producing a hardening effect on the metal; and if the hammering be continued

beyond this point, the metal fractures, not because it has been stretched to its limit of tenuity, but because its limit of compression has been exceeded.

Annealing.—The term should be confined to the relief of strain in metals produced by hammering, rolling, drawing, or by rapid cooling from a high temperature. The effect of the process of annealing is very marked in the case of gold plate struck up for a base-plate, already referred to. Once hardening has set in, which can be noted by the harsher ring produced by the stroke of the mallet, the metal is seen to yield less in response to the stroke. If at this stage, or preferably before, the metal is raised to a dull red heat and allowed to cool in the air, it is found to be comparatively soft and pliable, and shows little tendency to rupture if it receives moderate care. The lower the carat of gold, the more frequent is annealing necessary. Dental alloy, especially the grade containing 25 per cent. platinum, should usually be raised to a bright red, and kept at that heat for a few seconds. Alloys containing platinum generally require a higher temperature in annealing, and the alloy of gold and platinum as foil used for fused inlay matrices is much softer to work if raised to an almost white heat for one or two seconds. Examinations of micro-sections of gold before and after annealing seem to encourage the belief that in the hard state the molecular structure is drawn and attenuated, whereas after annealing the structure is seen to have recovered to the normal, by the molecules having contracted to their former proportions. The effects of annealing as seen on micro-section of alloys, such as steel, bronze, etc., are best studied from general textbooks. It may be briefly stated, however, as regards steel (the alloy of iron and carbon, as it is now regarded), that, compared with the hard state, annealing seems to disseminate the carbon particles more uniformly through the iron, the distribution of the carbon seemingly playing a most important part in the physical properties of steel.

Alloys as used for filling purposes for dental amalgams are generally subjected to a process of annealing after being cut to powder or filed to particles ready for use. Many authorities on the subject differ as to what temperature the alloy should be heated, and what length of time should be spent in the process. It is generally held that the effect of annealing is to lessen contraction in the finished fillings, and to increase the edge strength, resistance to attrition, etc. In annealing pure gold, as for filling purposes, the metal is best kept from contact with the naked flame of the spirit-lamp. This is especially applicable to cylinders, matt and fine foils. The electric annealers, the sheets of mica supplied with small portable stands, give excellent results, provided prolonged or over-heating is avoided. The practice common among many of the profession, of heating the gold at the naked flame, using the plugger point as the carrier, and using ordinary industrial methylated spirits, should be discouraged, as the other practice yields more satisfactory results. (See Gold.)

Tempering.—With the exception of steel, there are no alloys employed in dental metallurgy requiring tempering, and the subject has been dealt with under Steel. It is thought that, if steel be brought to a certain temperature, and cooled either in fat, oil, or water, its constitution remains the same, or nearly the same, as when the metal was strongly heated. Heat when applied to steel and the alloys of steel causes a rearrangement of the molecular structure. The extent to which this rearrangement takes place depends upon the temperature to which it is heated, and also the length of time the temperature is maintained; and if the tempering be effected at the temperatures as given already, or according to the colour attained by the steel, it will be noted how vastly different are the effects produced by even a slight difference of temperature.

#### CHAPTER XX

#### FURNACES AND CRUCIBLES

The Blast-Furnace.—It is only possible in these notes to give a brief outline of the main distinguishing features of each type of furnace, the special features which are considered necessary, such as the character of the linings, etc., having been referred to under the separate metals. The modern blast-furnace consists of a vertical shaft varying from 70 to 100 feet in height, with a width varying from 20 to 30 feet at the broadest part, which is situated where the furnace narrows down to the crucible or hearth, and known as the "boshes." The outer shell is of malleable iron, with an inner lining consisting of two layers of fire-clay, with an intermediate layer composed of fire-clay and coal-dust to overcome the effects produced by the expansion and contraction of the furnace walls during the operation. The ore, plus the fuel and fluxes, is charged into the furnace through an aperture in the upper surface of the furnace, and so arranged that the charge is equally distributed into the furnace, and the heated gases not allowed to escape. The twyers, or blowers, let into the side of the furnace near the level of the boshes vary in number from three to five, and the air to supply them heated from the waste gases from the furnace, which, after having been screened of dust, is brought to bear on the furnace charge at its hottest point. The heated air supplied under pressure greatly increases the temperature at this part of the furnace, completes the reduction of the metal, renders it more fluid, and facilitates its separation from the lime aluminates, etc., added to form a fusible slag. The twyers are made of iron, covered with fire-clay, and are kept cool by water circulating round them. The liquid slag is drawn off through an aperture formed by the removal of a fire-brick, situated slightly above the level of the liquid metal. Once the slag is removed, a taphole is opened on a level with the floor or hearth of the furnace, and the metal run into moulds, crucibles, ladles, etc.

The Reverberatory Furnace.—In this type of furnace the ore is separated from the fuel supplying the heat. It consists of a long fire-brick lined chamber placed horizontally, the floor or bed of which may be flat, slightly concave, or set in steps or ridges, the latter arrangement facilitating the preliminary roasting or calcining on the highest step or ridge, and by raking the charge down step by step the final reduction of the metal is effected on the lowest level towards the rear of the furnace where the heat is greatest. In the forefront of the furnace is placed the fire-grate containing the coal, coke, or charcoal, and separating it from the furnace is a raised step or ridge, known as the "fire-bar." The roof of the furnace slopes downwards towards the rear, with the result that when the flames and heat pass over the firebar, the slope on the roof causes them to be thrown down. or reverberated, upon the furnace charge, the hottest part of the furnace being towards the rear, where the final reduction of the metal is effected. A stack or chimney built at the rear of the furnace draws off the waste gases and products of combustion. Fresh charges of ore are introduced through hoppers let into the roof of the furnace. The furnace charge can also be distributed, raked, and rabbled by means of suitable openings let into the roof. The lining of the furnace varies according to the metal being prepared. As a rule the lining consists of fire-bricks built in, and such oxidizing materials as hammer scale, slag from previous reductions, etc., are laid over the fire-brick hearth. There may also be several fires built underneath the

furnace bed to insure complete reduction, greater heat, etc., the modifications being extremely numerous.

The Bessemer Converter.—The converter is a pearshaped vessel, varying in size from 8 to 15 feet in height, lined internally with about I foot of ground ganister, and externally with boiler-plates of malleable iron. The twyers or blowers, varying from six to twelve in number. consist of fire-clay cylinders, pierced at intervals with holes of \(\frac{3}{8}\) inch diameter, supplied with air-pressure during the furnace operation from 15 to 30 pounds. The converter is set upon trunions to permit of it being turned on its side for charging, cleaning, etc., and it is through one of these trunions that the air-pressure passes. The other trunion is solid, and by a rack-andpinion arrangement the turning or canting movement is effected. The ganister employed for lining purposes is a siliceous material resembling sandstone, but unlike sandstone it has the power of binding together when ground to fine powder and mixed with water. For description of the process, see Iron.

The Siemens or Open Hearth Furnace.—The modern form of this furnace consists of an oblong chamber, lined with Dinas bricks (a highly refractory substance), into which the ore or metal, and suitable oxidizing material, are charged. The heat is supplied from gas, produced from coal. The waste gases and heat from the furnace are led into chambers lined with fine fire-bricks, which bricks quickly absorb the heat, and are raised to a very high temperature. These chambers are supplied with valves, so that they may receive the waste gases, and heat and store them, and being heated, receive the gas from the producer and deliver it to the furnace. means of these regenerator chambers the temperature of the gas-flame is raised from 500° C. until it is delivered to the furnace at 1,500° C. and over, the temperature being raised, as it were, by a process of accumulation. The gas, as it receives additional heat from one chamber. is passed into the next, is raised by the temperature of that chamber, and so on through the series.

Modern Electro-Smelting Furnace.—Electro-smelting has been adopted with success for the reduction of cryolite and bauxite, both ores of aluminium, and more recently the process has been applied in Norway and Sweden for the reduction of iron ores and preparing steel. The underlying principles are the same. furnace is lined to a thickness of several inches with carbon, and the lining connected to the negative poles of a powerful dynamo. The ore is broken into small pieces and packed round carbon rods, which are connected to a copper frame joined up to the positive pole. The carbon rods at first are brought in contact with the carbon lining, and as the current flows are gradually withdrawn until an electric arc is formed, which, playing between the separated surfaces, raises the temperature at these points sufficiently to reduce the ores. The rods are gradually withdrawn as the ore is reduced and the bath becomes fluid. In reducing cryolite the carbon rods at this stage are allowed to dip into the molten aluminium when the oxide become electrolyzed; no electric arc from this point is allowed to form, the temperature of the bath being maintained by the conversion of the electricity into heat as it overcomes the electrical resistence of the bath.\* When the whole of the ore has been reduced, the electrical pressure suddenly rises, and on adding a further quantity, the voltage again falls, so that by drawing off the molten metal and adding fresh ore the process may be continuous.

**Muffle Furnaces.**—In these furnaces generally employed in dental laboratories for firing porcelain, staining teeth, cupelling gold, etc., the heat may be electric or gas. The muffle is prepared of fire-clay, and is generally flat across the bottom, with a curved roof resembling a D set thus  $\Omega$ . The back of the muffle is continuous

<sup>\*</sup> Huntingdon and Macmillan.

with the sides—closed in. The front is closed by a door cast of thicker fire-clay, with a mica panel let in to enable the muffle heat to be observed during a firing operation. The electrically heated muffles have the heating element, chiefly platinum wire, wound round the muffle body, and covered with a thin mix of fire-clay or investment body. The gas-heated muffles are fitted with a series of bunsen burners, spaced over the area covered by the muffle bottom to insure uniform heating. In no case where a muffle is employed is free access of air of advantage during the operation; the porcelain may be cracked, in cupellation process loss of metals through oxidation, and the muffle may be cracked by the ingress of cold air. The furnaces supplied with detachable muffles lend themselves to more rapid renewals and repairs.

The Injector Furnace.—Messrs. Fletcher, Russel, and Co., of Warrington, prepare several varieties of this useful type of furnace. It consists of a more or less circular body, composed of a dark fire-clay (resembling graphite with the binding of fire-clay in excess), about It inches in thickness around the circle, and wide and deep enough to admit the ordinary working sizes of crucibles. The central space for the crucible is shaped to conform to the outline of average crucible, with a small removable plate of fire-clay on which the crucible rests. The outer casing is of iron, and the furnace rests upon a shallow cast-iron stand to protect the work-table. The burner is of the blast type, the air-pressure being supplied or augmented by a foot-bellows, or from an airtank. The surface of the furnace opposite the burner is pierced with a hole wide enough to admit the flame, the space between the furnace and burner being such that the flame under pressure enters the furnace at its hottest, and slightly to one side of the centre. The effect of this arrangement is that the flame impinges upon one side of the interior of the furnace, and circulates around the crucible. This effects a saving in heat and in crucibles, as the heat is conserved and is brought to bear on the crucible equally over its surface. By closing the furnace with the fire-clay cover a very high temperature is quickly obtained suitable for meltings up to pure gold, heating investing rings for casting work, etc.

Fire-Clay Crucibles.—These crucibles are prepared in many shapes, sizes, and in many degrees of fineness, from the fine fire-clay crucible almost white in colour. suitable for melting fusible alloys, to the coarse brown variety suitable for high temperatures, as in preparing aluminium bronze, etc. The base for all the varieties is ground fire-clay. In the finest and whitest varieties the clay alone is employed, and in the stronger the clay is mixed with burnt clay, for which old crucibles are employed. The choice of a crucible for dental work will be governed by the metal or alloys being treated. Copper, for example, gives off an oxide which corrodes the fine clay crucibles, and the variety known as "London round" is extremely strong, and withstands corrosion for a considerable time. The variety known as the "Salamander," and prepared from graphite mixed with fire-clay as a binding material, is almost black in colour, extremely strong and dense, and is well adapted for melting gold or silver, and their alloys. Fire-clay crucibles should be annealed before using, and where precious metals are being melted, rubbed with charcoal to insure the metal running clear of the crucible. The annealing is carried out either in an open furnace or the injector type, by placing the crucible in the inverted position and raising it to a bright heat, and allowing it to cool slowly.

Carbon Crucibles.—These crucibles are prepared from carbon, as the name implies, with a binding material. They are of great use in carrying out experimental work, where checking for accuracy is desired, and are said to reduce the oxidation of readily oxidized metals, such as tin, zinc, etc. They are brittle and more friable

than the fire-clay varieties, besides being more expensive to renew.

Electric Crucibles.—These crucibles as supplied for dental purposes consist of a furnace of fine fire-clay large enough to contain a crucible to melt from I to 16 ounces of metal. The temperature reached is sufficient to melt pure gold. The heating element is of platinum wound round the crucible walls, and the furnace is worked in conjunction with a resistance-board for the raising and lowering of the temperature. There is also a variety employed for lower meltings (not exceeding 1,000° C.), supplied with the furnace, made of thin fused silica, which contains the platinum wire fused into the walls. The crucible itself is separate from the furnace, and may be of any of the materials supplied—fire-clay, plumbago, or carbon. The outer casings are of nickel. In all varieties of electric crucibles the heat should be raised gradually and reduced gradually, contact with currents of cold air being carefully avoided to reduce the risks of cracking the walls. The variety mostly in use has the walls of fire-clay, as cracks appearing can be quickly repaired by running in some fine fire-clay mixed thin with water when the crucible is cold. Electric furnaces and crucibles are best worked in conjunction with thermo-couples to insure accurate temperatures. Messrs. John Griffin and Sons, London, have a large variety of electric furnaces and crucibles suitable for dental work not usually illustrated in dental magazines.

#### CHAPTER XXI

#### PYROMETRY

When the fusing-points of the different metals are under study, it will be seen that at times there are wide variations in the figures given by the different writers, even for the same metal. This in the past has been due to the figures being taken of the melting-points of impure metals, and also to the absence of any reliable

method of determining high temperatures.

At the present time the methods available for registering temperatures, though they may vary widely in principle, are generally sufficiently accurate for the figures given to be accepted, the difference between authorities generally being in the expression of a decimal fraction. As early as the eighth century we find that Geber\* held the view "that heat could not be measured, and that consequently great difficulty attended operations requiring heat"; and the same view seems to have held good for another ten centuries. Wedgwood, of Wedgwood ware fame, saw that it would be much to his advantage, and the bettering of his products, if his workmen had some reliable means afforded them of keeping a check on the heat of the furnaces and ovens, and from his experiments gradually developed the modern system of pyrometry. He clearly saw the importance of being able to distinguish the gradations between the bright red heat and the blazing white heat that some of his ware had to be raised to. His early attempts were confined to watching the contraction of

<sup>\*</sup> Sir W. Roberts-Austin, "Introduction to Metallurgy."

various clays when strongly heated, marking their change of shape, etc., until he had reached a practicable working basis. At present there are innumerable devices em-

ployed to register temperatures.

The thermometer is too well understood to require more than mention, but very high temperatures cannot be registered by its use. Pyrometers, on the other hand, are intended to register temperatures beyond those possible by the ordinary thermometer, and vary in construction according to the various purposes to which they are applied.

For use with electric furnaces for fusing dental porcelains, the pyrometer generally used is the thermocouple. The use of this instrument depends upon the fact that, if two dissimilar metals joined together at one end are heated, a current of electricity is produced, and that this current is nearly proportional to the temperature, and can be measured by the deflections of a dead-beat galvanometer. This galvanometer may be of the mirror form, or may be provided with a dial and pointer. The scale on this dial is calibrated from known and definite melting-points.

The use of the thermo-junction appears to have been first suggested by Becquerel in 1826, and was adopted by Pouillet some ten years later. At first the metals forming the thermo-junction were badly chosen, and at a later date Professor Le Chatelier advocated the use of platinum in conjunction with platinum alloyed with 10 per cent. rhodium. Barns, on the other hand, alloyed the platinum with iridium, as suggested by Tait, obtaining good results even at very high temperatures.

**Dental Pyrometers.**—These instruments are generally of the thermo-junction type, the variations being confined to the manner of attaching them to the electric furnace. Some have the thermo-junction loose, to be laid on the floor of the furnace, while others have it embedded in the fire-clay walls of the furnace. Both of these types may be held open to objection. The loose

form is likely to record the temperature of the furnace nearest the door, as the tray holding the porcelain to be fused will occupy the greater part of the area at the back, where the heat is generally greatest. When the junction is embedded, it is less accessible in the case of repairs being necessary, either to the junction, the electric wiring of the furnace, or to the muffle walls.

The thermo-junction consists of two wires, one of which is of platinum, the other an alloy of platinum with 10 per cent. of rhodium or iridium. These are soldered together only at the end in contact with the heat, and connected with a dead-beat galvanometer of about 200 ohms resistance. The temperature is recorded on a scaled dial on the galvanometer, which may be of the suspended type, quite separate from the electric furnace; may be built in on the same base as the furnace; or may be loose to hang to a wall or bracket, etc.

These pyrometers are intended to register temperatures up to 4,000° F., such as are required for fusing high-grade porcelains. In using pyrometers in fusing porcelain, as in inlay and continuous gum-work, where porcelains of different fusing-points are employed, and where in the preliminary firings it is only essential to raise the heat sufficiently high to give the porcelain a biscuit glaze, and cause it to reach its ultimate contraction, exact temperatures are absolutely essential to produce good results. It is found in practice that pyrometers are more accurate if the current of electricity is admitted gradually to increase the temperature slowly, and that, once the desired temperature is reached, the furnace should be allowed to cool before reheating. practice of allowing the current to remain on until the second or subsequent firings have been completed interferes with the electrical disturbance set up in the thermo-junction; and the readings on the dial are less reliable.

When the temperatures required are not so high, the thermo-junction varies in composition. Thus, where

1,800° to 2,090° F. is the highest desired, the thermojunction may be nickel and steel, as made by Messrs. Crompton and Co. In this pyrometer, a nickel rod runs down the centre of a steel tube without touching it, except at the extreme end, where the two metals are welded together. The couple is in connection with a recording galvanometer, as in the case of those pyrometers described. There are many modifications of electrical pyrometer, which are used chiefly in iron and steel works. In the Siemens electrical pyrometer acidulated water is decomposed both by the current from the junction and from the resistance coil, the difference in quantity decomposed between the junction and the resistance affording a means of registering temperatures.

Sir W. Roberts-Austin produced a pyrometer by means of which continuous records of temperatures can be obtained by means of sensitized paper on a revolving drum, much in the same way as differences of temperatures and air pressures are recorded by self-recording

aneroid barometers, etc.

Le Cron's Pyrometer Pellets.—For dental purposes where occasional firings, as with porcelain, are undertaken, the series of alloys introduced by Dr. Le Cron in the form of rounded beads is extremely useful. They can be obtained covering a wide range of temperatures (2,000° to 3,000° F.), to suit the fusing-points of the

best-grade porcelains.

Method of Use.—A bead of the alloy is chosen whose melting-point coincides with the fusing-point of the porcelain to be used. It is placed in the circular opening in the top of a small open-sided crucible stand made for the purpose. This is then introduced into the furnace with the inlay or piece of continuous gumwork. When the temperature reaches the melting-point of the alloy, the bead becomes liquid, and drops through into the concave base of the crucible or stand, and the porcelain is found to have fused.

# REPORT ON THE STRUCTURAL AND OTHER CHANGES ARISING IN CONNECTION WITH METALS USED IN THE MOUTH.\*

In studying the changes arising in metals used by the profession, the first fact to impress us is that these changes are not constant. For example, a metal as employed as a base for a denture where no teeth are present in the mouth may present an entirely different appearance compared with the same metal when employed as a base for a partial denture, portion of a bridge, etc., where other metals and alloys are present in the same mouth. It will be necessary, therefore, in submitting this report, to distinguish in each instance how the metal or alloy behaves in an edentulous mouth; its effects upon the tissues in relation to it, and also its behaviour when in close relation to other metals or alloys.

Generally speaking, the metals employed by the profession are present in the mouth in the pure form, by which I mean that even when present as constituents of alloys they are the purest obtainable—for example, a piece of r8-carat gold will be composed of pure gold, pure copper, and pure silver. By assuming this to be true—and I have it on the authority of several of our sources of supply that it is true—we are enabled to exclude from the scope of this report the probable effects of many metals and metallic salts which would be capable of making their presence both seen and felt if present as impurities.

<sup>\*</sup> Delivered at the Sixth International Dental Congress, London, 1914, Section IV.: Dental Physics, Chemistry, Radiography, and Metallurgy, by W. Bruce Hepburn, L.D.S., Glasgow.

Gold.—Taken all over, I think that at present gold is the most extensively used metal by the profession, so that I will consider it first in order. Gold in the pure form of 24-carat of 1,000 fineness is met with as fillings, as thin linings on vulcanite dentures, on the outer shell of crowns and collars, and certain abutments for bridges, inlays, etc. As a lining for vulcanite dentures, it retains its colour in edentulous mouths where the saliva is normal. The mucous membranes are benefited by its presence, and in instances where vulcanite itself fails to give comfort from sponginess of the tissues, or where there exists a distinct tendency towards irritation followed by ulceration, pure gold linings in the majority of cases affords a reliable means of relieving the condition. In excessively alkaline salivas the metal is discoloured, and can only be kept bright by daily polishing. Where biliary symptoms are present, the darkening of the metal closely resembles the formation of a sulphide, but in all conditions of the saliva there is no loss of metal by solution or other means, or formation of any salt of gold leading to loss of metal.

Where other metals are present, such as amalgam fillings, the changes are influenced in a fairly definite ratio by the presence of copper, zinc, and mercury. example, a partial vulcanite denture, gold lined, and in contact with a tooth filled with Sulivan, or copper amalgam, is discoloured at that point, the discoloration closely resembling a dark copper oxide. The same denture, if in contact with amalgam, containing, say, silver, tin, copper, and zinc, the discoloration is less dark, but tinged with grey. The same denture, if in a mouth where no amalgams are present, remains under the same condition as in the edentulous mouth—namely, that it

is influenced by the saliva only.

Dentures of 18-carat gold in edentulous cases follow very much the same rules as those linings of pure gold, and also where amalgam fillings are present the darkening is present, and where they are absent the colour is better. A denture made from 18-carat flat gold, and swaged, remains a better colour than one made from the same carat of gold and cast, and this happens under all conditions. Also, a denture cast and properly annealed, and gently hammered all over on a Babbit metal die, darkens less on the hammered surface than on the cast surface. The only explanation I dare put forward is that the rolled metal has its molecular structure changed in such a manner that the preponderance of gold in each mixed crystal is capable of protecting the silver and copper to a greater extent than in the irregular crystal of the cast metal.

So far as my observations have gone, the presence of platinum in gold for dentures and clasps, while increasing the elasticity of the alloy, does not lessen the oxidation of the surface. One or two forms of 17-carat platinized band gold were more affected than 18-carat ordinary band gold. Very much the same effect may be observed in the platinized foils sometimes employed for surfacing gold fillings. There is more darkening of the approximal surface than in the filling made from 1,000 fine gold. The matt consisting of gold, plus platinum, etc., as employed for fillings, exhibits this darkening even more so than gold and platinum foils.

I will defer the consideration of fillings, crowns, etc., until the metals used as bases, etc., have been considered.

Platinum and its alloy, iridio-platinum, are so seldom found exposed to the saliva that it is hard to obtain sufficient data to draw conclusions, but it may be considered safe in assuming that they will darken less than pure gold, even when in exposed positions, and be less affected by amalgam fillings yielding mercury.

Silver and Platinum Alloy.—The alloy of silver and platinum known in Britain as dental alloy, and containing anything from 10 to 35 per cent. platinum, and the balance silver, seems to be falling into disuse, chiefly on account of its enhanced cost—a cost which is not in proportion to its worth as compared with the

16 and 18-carat gold for the same purposes. This alloy was employed for the same purposes as flat gold plate of 18 carat, and is of a greyish-white colour when freshly polished. In edentulous mouths its use was restricted to upper base plates, as the alloys containing the higher percentage of platinum were harder to swage without fracturing than gold. In many mouths it disclosed a marked darkening on the lingual surface of the palatal base, even in cases where the saliva was neutral and slightly acid. Many cases were less affected on the surface next the palate, pointing almost to the conclusion that foodstuffs and liquids being taken acted more rapidly upon the alloy than the normal saliva of the patient. The tissues remained normal.

Frequently gold and platinized gold bands were soldered to the alloy when employed for partial dentures, the solder generally being 12 to 15 carat gold solder. have found more trouble from galvanic action in mouths where this alloy was employed than any other as a baseplate metal. A glance, meanwhile, at the combination of metals in such a case will be sufficient to indicate this. In the dental alloy, silver and platinum; in the band metal, gold, silver, copper, and sometimes platinum; and in the solder, gold, silver, copper, and a trace of zinc. Place these in the same mouth as a copper amalgam filling, and not necessarily in contact, and the symptoms

are at times quite exhibitanting.

Dental alloy does not behave constant in its physical properties. One great difficulty is the tendency towards brittleness, especially in dentures to be repaired; and the solvent action upon the lower grade alloys of a pickling solution suitable for 16-carat gold. Examination of several samples of this alloy have satisfied me that where less than 30 per cent. platinum is present, these defects are more marked, and oxidization is increased. The dissemination of the platinum through the silver is not constant, and frequent and careful annealing during swaging fails at times to prevent fracture.

Aluminium and its Alloys.—Pure aluminium rolled in sheet and swaged (care being taken to employ a Babbit metal die, and a tin counter die) behaves in a more constant manner than when cast. In edentulous mouths of normal saliva cases have been examined after five years, and found giving good results both as to the metal's effect upon the mucous membrane and the appearance of the metal itself, which remains clean and free from darkening, even in deep palates and rugæ. Where the saliva is distinctly alkaline, its behaviour varies. One cast upper denture examined was exceedingly rough, and pitted upon the portion of the palate posterior to the suction disc. This was certified as wastage of the metal from its appearance when inserted, and with the rest of the plate, and this within two years of its insertion. Another base-plate struck from flat sheet became perforated in the same region within thirty months of insertion. The cast denture was in an edentulous mouth, and the struck plate in one with lower teeth in position, but no fillings present. A denture lately since came under my observation, prepared of cast aluminium and silver. There were several amalgam fillings in position in some lower teeth. The saliva was acid to litmus-paper, and this denture, close upon two years old, was dark and offensive. The patient, an intelligent Canadian, stated that he left the plate intentionally unscrubbed, as he had a peculiarly steely taste in his mouth for some time after polishing the surface of the metal. I made tests for galvanic action between fillings and the plate, using the ameter of an ionic outfit; but beyond a very slight waver of the needle, and the consciousness on the part of the patient of the steely taste, there were no definite results to be obtained. I certainly expected he would have experienced shock, especially in a large contour molar filling, but the pulp may have been guarded by cement, or possibly dead. All the fillings except one, recently inserted, showed changes in condition.

From my observation of aluminium and its alloys, and keeping in view the fact that the metal exerts its electro-positive properties even when alloyed, I am of opinion that the choice of mouths suitable for these is extremely limited, and in the most suitable cases, even then the metal and its alloys should be gilded from time to time.

Aluminium bronze 5 per cent. I have had to discard, as it was open to the same objection as the aluminium alloys, even when employed for temporary purposes in mouths where copper amalgam and silver-tin amalgam were in position. The bronze oxidized badly, and galvanic action was intensified.

Victoria metal, the alloy of a golden-vellow colour, and containing nickel, copper, and zinc, became perforated in one instance in less than one year from date of its insertion. The fillings present were cements and amalgams, and there was a considerable wastage in all. The saliva was slightly acid. From my experience in several such instances I have ceased using these alloys as base-plate metals, as I have so far been unable to establish a regular set of conditions where one may say definitely that good results will accrue. From the metallurgist's point of view, aluminium, zinc, antimony, and magnesium are base-metals capable of exerting their influence even when alloyed. If this is accepted, then I am of opinion that these metals should be eliminated from the mouth, or employed as constituents of alloys for temporary purposes only.

If we consider mouths where partial dentures and several varieties of fillings are present, the results obtained are at times so perplexing that it becomes extremely difficult to draw an accurate inference from what is presented. For example, why should there be present intense galvanic action between dissimilar metals in one mouth, accompanied by erosion, recession of the gum, and unsatisfactory results generally from work done in the mouth, in some cases, and comfort and good results under almost similar conditions in others?

Why should a gold crown articulating with an amalgam filling in one case be accompanied by galvanic action and frequently pulp trouble, and in others quiescence?

Why should a partial 18-carat gold or dental alloy denture become tarnished in an otherwise clean mouth, and in another less careful mouth remain quiet clear

and bright?

These are a few of the questions which I have put to myself, and had them put to me, and they are difficult to explain. In the list of instructions submitted to reporters to this Congress we are advised not to employ theories, but to keep to hard and cold facts, by presenting the subject as it is. By taking advantage of this last part of the instructions, I shall be saved from the necessity of explaining my own queries; and by presenting to you what I have learned and observed, you will necessarily be left to draw your own conclusions.

I think it will be admitted that our greatest difficulties are presented in mouths where there are several metals in position, as in edentulous mouths the conditions are much more constant and more readily understood.

Fillings.—As a rule the complexity is produced by the presence of different kinds of fillings, each filling having been selected as the most suitable or convenient for the cavity as it occurs. When a filling is inserted, we are generally presupposing that our work will be permanent—at least, as far as the individual concerns us—excepting those cases, of course, where the caries has extended so far as to lead us to hope for a moderate continuation of usefulness of the tooth previous to crowning.

Taking amalgams, there are certain general changes

which occur after the filling has been in position for some time which cannot be explained as entirely due to expansion, contraction, or spheroiding. For example, cases occur where an amalgam filling under observation at regular periods suddenly discloses changes in its relationship to the cavity walls which cause it to be condemned. Industrially, alloys are employed which remain constant in their behaviour as regards their physical properties; are exposed to thermal changes, friction, strain, and the test of time, and do not exhibit the inconstancy I refer to. The alloys which we employ as amalgams contain metals which, if we except zinc, are insoluble in human saliva, and are confined, if we except copper amalgam, to silver, tin, and mercury, with copper, zinc, gold, and platinum added as modifying metals. Examination of these metals, taken singly in the pure state, or in alloys (with the exception of zinc), and immersed in normal human saliva, shows that no change of volume occurs. An examination, on the other hand, of many amalgam fillings which have been in position and giving service for several years, it may be, exhibit well-defined changes, such as expansion or contraction, spheroiding and roughening, or a condition resembling erosion in its character. All these changes have been observed for years, and we are still attempting to solve the riddle.

I wish it to be clearly understood at this stage that I am confining my remarks to those mouths where we have consistently been able to do our best work, and where the patient had kept the teeth regularly brushed and the mouth free from septic roots. By doing this, we will avoid the question of bad cavity preparation, and its attendant veils, and lack of cleanliness on the part of the patient. A badly prepared cavity in a dirty or a clean mouth brings its own retribution within two years of insertion. Everyone is more or less familiar with the mouth in which gold fillings never remain a good colour, these being generally brownish in appearance, and this intensified in approximal spaces. A brisk buffing with precipitated chalk quickly removes this, and the surface of the metal may be smooth and regular. Personally, I had always explained this to myself as due to fruit stains, excess of sulphuretted hydrogen, or in some cases to faulty use of the brush, etc.

For some time past I have taken notes from my close examination of such cases, and my results are as follows:

I. The darkening of the fillings is present in mouths

both alkaline and acid to litmus-paper.

2. In mouths which are carefully attended to by the patient, the difference being that the darkening was generally confined to positions not readily accessible to the brush.

3. Is never present in mouths where gold is the only metal employed for fillings or crowns.

4. Is present where copper amalgam filling has been

used to restore lost tooth tissue to any extent.

5. Is present where German silver is present as part of apparatus for treatment of malocclusions, even when no amalgam fillings are present.

Then, again, my notes on the examination of amalgam

fillings give me the following results:

- r. In young patients, when copper amalgam alone is employed, the amalgam fulfils its function admirably, does not wash out, expand, contracts little, and recurrent decay in cavities, underlined with cement, absent.
- 2. Where copper amalgam is employed for the molar region and gold for the incisors, washing out of the amalgam is present, and frequent failures of the gold in cervical regions, with darkening.
- 3. Where amalgam, and not necessarily copper, is employed in anything like close proximity to gold fillings, both fillings are defective.
- 4. Where inlays of 20 and 22 carat gold are similarly placed, the results are better.
  - 5. Where inlays of silver-tin-copper or gold are in

contact with gold fillings, crowns, or inlays, no change

is apparent.

6. In cases where I have only employed a so-called "gold amalgam" in the molar region, and gold in front, the destruction is very much reduced.

7. Where dentures of aluminium, aluminium-bronze,

or Victoria metal are present, all fillings suffer.

In compiling these results, I have purposely avoided those cases of rapid destruction following upon a gold filling or crown articulating with, or actually in contact with, an amalgam filling, as I think I am justified in saying that where such can be avoided, it is better practice. Mercury will draw to gold, even from an old amalgam filling, with mutual harm to the gold and amalgam. Cases do present themselves where gold has been built upon an amalgam foundation with success, but in such cases the amalgam has been mixed with little or no excess of mercury, and is allowed to set before adding the gold. What little mercury attacks the gold is confined to the layers directly in contact with the amalgam, and shows in successful cases no signs of spreading through the filling.

If we admit the general correctness of these two groups of results, I think we may safely make one or two general conclusions, and the first is that we should avoid complexity as far as possible in inserting metals in the mouth. By carefully scanning the work already done in a given mouth, and considering what relation the new work we are about to do will stand in relation to it, we are enabled in many instances to avoid complexity, and at the same time stand to improve our results. For the past seven years I have been adopting this rule, and by charting up the class of filling inserted in each instance, I can observe their behaviour. If amalgams are indicated, I make the restoration with the same amalgam, and never do I employ copper amalgams to any extent in a patient over fourteen years with a clean mouth. When large restorations are necessary, hollow inlays of gold or silver 73 parts, tin 23 parts, gold 2 parts, and copper 2 parts, yield better results than copper

amalgam in mass.

Looking to the cause of many of our failures, I am of opinion that as a profession we shall have to remould our ideas to a great extent as to our filling operations. Amalgams yielding perfect theoretical results, and perfect as to laboratory tests as to expansion, contraction, edge strength, etc., very frequently fail when tested in the mouth, while many alloys prepared for amalgams theoretically wrong (being very little short of mechanical mixtures of the several metals with mercury as the cementing agent) have given good results, and that over a long period of years; whereas, on the other hand, I have still to find a case where the true silver-tin alloy gives permanent results, while alloys with the addition of copper or gold, or copper and gold, are giving good results.

The determination of the cause of the apparent wastage or "solution" of metal fillings in the mouth is

far from being definitely answered.

In alloys as used industrially, as in engineering—for instance—we never find two groups of alloys, or any combination of single metals, brought together into working parts which would react the one upon the other, or, in other words, which would behave as electropositive and electro-negative one to the other, as failure to guard against this would mean wastage of the metals in contact. Applied to our work, I am of opinion that bringing such metals as zinc and copper together in the mouth is inadvisable. Zinc is added to certain proprietary alloys to hasten the setting and increase the whiteness; copper to increase edge-strength and reduce oxidation. If the effects of these two metals were confined to the amalgam or alloy containing them, we would reckon on the proportion of each required to produce a desired result, but from the results of many tests it is known that each metal contained in an alloy or amalgam,

unless when in perfect solution with another metal or metals, continues to exert its influence on the physical properties of that alloy or amalgam for an indefinite period, over and above which it still retains its power of influence as an electro-positive or electro-negative.

I am also of opinion that it is the power possessed by the separate metals to exert their electric properties that accounts for much that is mysterious. I had hoped to have presented a series of scales of results made by testing for galvanic action between metals in the mouth. The ameter I possess, I discovered too late, required fully  $\frac{1}{2}$  milliampère to move the needle, and the average shock experienced as between fillings, when pronounced, only caused the needle to wayer. I intend carrying out some tests with a galvanometer of the mirror type with some definite scale indexed on the glass to go by, and hope to have the pleasure of presenting these results to the profession.

The darkening on gold fillings, crowns, dentures, etc., consists mainly of metallic copper, while the corrosion of retaining bands, clasps, etc., made of German silver, point in both instances to a depletion of metallic copper, with zinc exaggerating the action in the case of German silver.

The silver-tin amalgams, while behaving much better than copper amalgam, become very irregular on the surface after a few years, and have every appearance of diminution in bulk by the loss of some constituent metal, and can readily be cut with a dentin bur. The cause of this is hard to find, unless we can trace the destruction as coming from other fillings present in the mouth, free mercury, or free tin becoming oxidized and being washed out by the saliva. Inlays made from the same formula as the silver-tin amalgam give good results, while the addition of a trace of copper and gold, while theoretically unsound, gives still better results.

The patient's habits certainly influence our work, as, for instance, the difference between a clean, well-kept mouth, and a dirty one which seldom if ever receives the attention of a brush. The manner of feeding, whether the food is taken soft and swallowed without the necessity of mastication; or where the food is taken as dry as possible and receives efficient mastication. In the mouths of the hard chewers almost any class of filling material will serve well, provided it possesses sufficient edge-strength, whereas in the majority of soft feeders almost any class of work requires careful and constant supervision. The so-called "iron tonics," I consider, affect our work in many instances in a manner we seldom imagine. I have in mind an instance of where a group of silicate fillings, underlined with an oxyphosphate of zinc cement, remained a beautiful colour, and wore almost as advertised until the patient went through a course of iron tonics. These fillings were ruined in colour, and washed out rapidly. Amalgams suffer after a prolonged course of such tonics, but less so than cements and silicates; while gold fillings, apart from a surface darkening which disappears when brushed, show no change in volume.

Metal dentures are affected in very much the same manner as fillings, and the same acids will attack the metal or alloy in the mouth as attack it in laboratory

tests.

One always has to allow so much for the personal equation of patient and operator that anything approaching dogmatism on any one point is impossible. Even where an operator can seriously examine his results extending over several years, and in mouths which he has regularly under inspection, such results, while affording him valuable assistance, would not justify him in becoming positive or dogmatic, as to like results following another operator.

In what I have stated in this report I have attempted to bring before you the results of my observations of normal cases. There are many cases which are presented where some metal or alloy has come far short of expectations, and where the probable cause is so obscure as to place it in the realm of theories. Such I have purposely avoided, as in the report we should endeavour to find some common ground of agreement, and discuss the question to our mutual benefit.

## APPENDIX

### TABLE OF ALLOYS.

Aich's Metal	••	• •	Copper 60 to 70, zinc 38.2, iron 1.8, per cent.	
Aluminium Bronze	(1)	••	Copper 95, aluminium 5, per cent.	
Aluminium Bronze	(2)	••	Copper 90, aluminium 10, per cent.	
Aluminium Gold	••	• •	Gold 78.48, aluminium 21.52, per cent.	
Aluminium Silver	••	••	Copper 70, nickel 23, aluminium 7, parts.	
Aluminium Tin			Aluminium 100, tin 10, parts.	
Arguzoid			Copper 56, nickel 13.5, zinc 23,	
_			lead 3.5, tin 4, per cent.	
Babbit Metal (1)			Tin 66, antimony 22.3, copper	
			11.1, per cent.	
Babbit Metal (2)	••	••	Tin 24, antimony 8, copper 4, parts.	
Haskell's	••	• •	Tin 8, antimony 2, copper 1, parts.	
Fletcher's	••	••	Tin 70.6, antimony 17.64, copper 11.76, per cent.	
Bean's Alloy			Tin 95, silver 5, parts.	
Bell Metal			Copper 80, tin 20, per cent.	
Blue Gold			Iron 75, gold 25, per cent.	
Brass	••	• •	30 to 40 zinc, copper 60 to 70, per cent.	
Sheet	• •	• •	Copper 70, zinc 30, per cent., and a trace of lead.	
Casting	• •	• •	Copper 47, zinc 50, tin and lead, 3, per cent.	
Britannia Metal (1)	••	• •	Tin 42, antimony 3, copper 1, brass 1, parts.	
Britannia Metal (2)		• •	Tin 90.7, antimony 7.8, copper	
			1·5, parts.	
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Carrol's Alloy	• •		Aluminium 98, platinum, silver, and copper 2, per cent.
Crown Gold			Gold 22 dwts., silver 18 grs.,
olown dole	••	••	copper i dwt., platinum 6 grs.
Dental Alloy (1)			Silver 75, platinum 25, parts.
Dental Alloy (2)		• •	3 to 15 grs. platinum per dwt. of silver.
Dorrance's Alloy	••	• •	Copper 6, silver 2, zinc 4, parts.
Dutch Metal	••	• •	Copper 84.6, zinc 15.6, per cent.
Electrum Metal		••	Copper 51.6, nickel 25.8, zinc 22.6, per cent.
Fusible Alloys:			·, <b>r</b> · · · · · · · · · · · · · · · · · · ·
Brophy's	••	• •	Bismuth 12, tin 10, lead 11, parts.
Crouse's		••	Bismuth 8, tin 5, lead 5, cadmium 1, parts.
Fusible (1)			Bismuth 3, tin 2, parts.
Fusible (2)		••	Bismuth 48, tin 26, lead 19, cadmium 13 parts.
Fusible (3)		• •	Bismuth 4, tin 12, lead 15, parts.
Lichtenberg's		• •	Bismuth 7, tin 7, lead 13, cadmium 2, parts.
Lipowitz's	• •	••	Bismuth 15, tin 4, lead 8, cadmium 3, parts.
Molyneaux's	••		Bismuth 5, tin 2, lead 3, cadmium 2, parts.
Newton's			Bismuth 8, tin 3, lead 5, parts.
Rose's		• • •	Bismuth 8, tin 3, lead 8, parts.
Wood's			Bismuth 5, tin 2, lead 4, cad-
			mium 2, parts.
Gold Alloys:			, <b>F</b>
22 Carat	••	• •	Gold 22, silver 1, copper 1, parts.
21.6 Carat (1)	••	••	Gold 90, silver 5, copper 5, parts.
21.6 Carat (2)			Gold 50, silver 5, coin gold 45, parts.
20 Carat for Ba	se-pla	tes	Gold 20, silver 2, copper 2, dwts.
20 Carat Platin	ized (1	)	Gold 20, silver 1, copper 2, platinum 1, dwts.
20 Carat Platini	ized (2	)	Coin gold 20 dwts.; silver 10, copper 8, platinum 10, grs.
18 Carat for plates (1)	r Ba	se-	Gold 18, copper 4, silver 2, dwts.
18 Carat fo plates (2)	r Ba	ise-	Gold 18, copper 3, silver 3, dwts.

Gold Alloys—continued:	
18 Carat Platinized (1)	Gold 18, copper 1, silver 4,
	platinum 1, dwts.
18 Carat Platinized (2)	Gold 18, copper 3, silver 2, platinum 1, dwts.
17 Carat Platinized	Gold 17, copper 4, silver 2, platinum 1, dwts.
16 Carat Platinized	Gold 24, copper 2, silver 1, platinum 1, dwts.
16 Carat for Base-	Gold 16, copper 4, silver 4, dwts.
plates (1) 16 Carat for Base-	Cold II durts coppor a durts 6
plates (2)	Gold 11 dwts., copper 2 dwts. 6 grs., silver 4 dwts. 6 grs.
Gun Metal	Copper 90, tin 10, per cent.
Hall's Metal	Nickel, copper, zinc, and another element.
Kingsbury's Alloy	Tin 16, antimony 1, parts.
Kingsley's Alloy	Tin 16, bismuth 1, parts.
Levol's Homogenous Alloys	718.93 parts silver per 1,000 parts copper.
Magnalium	Aluminium plus magnesium
Mannneim Gold	Copper 75, zinc 25, per cent. Tin and lead in equal parts,
Motor Motor	with a trace of antimony.
Mosaic Gold	Copper 50, zinc 50, per cent.
Muntz Metal	Copper 64, zinc 36, per cent.
Nickel Silver	Copper 5, nickel 2 to 3, zinc 3.5, parts.
Nickel Silver as in Plate	Copper 5, nickel 2, zinc 3, parts.
Pewter Metal (1)	Antimony 15, lead 6, tin 79, per cent.
Pewter Metal (2)	Tin 12, antimony 3, parts.
Phosphur Bronzé	Phosphorus 0.25 to 3, tin 5 to 15, per cent., and the remainder copper.
Pinchbeck's Alloy	Copper 90, zinc 10, per cent.
Platinum Solder	Gold 75, platinum 25, parts.
Platinoid (1)	Copper 60, zinc 24, nickel 14, tungsten 2, parts.
Platinoid (2)	Copper 60.50, nickel 15.97, zinc 23.00, lead 0.12, iron 0.35, cadmium 0.12, per cent.
Reese's Alloy	Tin 20, silver 5, parts.
Steels: Aluminium Steel	Not more than 1 per cent. alu-
Chrome Steel	minium. From 0.25 to 2 per cent. chro-
Manganese Steel	From 6 to 14 percent, manganese

Steels—continued:
Nickel Steel From 2 to 4 per cent. nickel, and 0.2 to 0.3 per cent. car-
bon. Silicon Steel Similar to aluminium steel.
Tungsten Steel 2 to 7 per cent. tungsten added
to 2 to 3 per cent. steel.
Solders: Aluminium Solders:
Aluminium Solder (1) Aluminium 20, zinc 80, parts.
Aluminium Solder (2) Aluminium 8, zinc 92, parts.
Common Solder Copper 4, aluminium 6, zinc 90, parts.
Hard Solder ) (Cold 88.8 silver 4.68 conner
1:07 Am- 6:44 per cent.
Medium Hard   minium   Gold 54.40, silver 27.00, copper
Solder (18.00, per cent.
Platinum - Aluminium Gold 30, platinum 1, silver 20, Solder (Schlosser) aluminium 100, parts.
Gold-Aluminium Solder Gold 50, silver 10, copper 10,
aluminium 20, parts.
Hard Solder Pure block tin from 90 to 98
parts, bismuth from 1 to 5
parts, aluminium from 1 to 5
Soft Solder (Frismuth) . Pure block tin 90 to 99, bismuth
I to 10, parts.
Thowles's Solder Tin 55, zinc 23, silver 5, alu
minium 2, parts.
Solder for Trays, etc. (1) Zinc 62.5, tin 25, lead 12.5, per cent.
Solder for Trays, etc. (2) Cadmium 50, zinc 20, tin 30,
parts.
Fine Solder I part lead to 2 parts tin.  Gold Solders:
22 Carat Solder Pure gold 22, brass 2, grs.
20 Carat Solder, or Pure gold 20, zinc 1½, silver
No. oo (1) solder 3, grs.
20 Carat Solder, or Pure gold 5 dwts., pure silver No. 00 (2) 12, copper 6, grs.
No. 00 (2)  12, copper 6, grs.  20 Carat Solder Pure gold 20, Dorrance's alloy,
4, dwts.
18 Carat Solder, or No. 1 Coin gold 30, pure silver 4,
(I) pure copper I, brass I,
parts.  18 Carat Solder, or No. 1 Coin gold $19\frac{1}{2}$ , pure silver $2\frac{1}{2}$ ,
(2) pure copper 1, brass 1,
dwts.
16 Carat Solder, or No. 2 Pure gold 11 dwts., pure silver
3 dwts. 6 grs., pure copper
2 dwts, 6 grs,

Solders: Gold-continued:	
16 Carat Solder, or No. 2	Pure gold 11 dwts. 12 grs., pure
(2)	silver 3 dwts., pure copper
	1 dwt. 12 grs., pure zinc 12 grs
15 Carat Solder (Jeweller's)	Pure gold 15, pure copper 5,
(I)	pure silver 4, dwts.
15 Carat Solder (Jeweller's)	Standard gold (22 carat) 16½
(2)	pure copper $3\frac{1}{2}$ , pure silver 4, dwts.
15 Carat Ordinary (1)	Pure gold 15, pure copper 4,
"5"	pure silver 4, brass 1, dwts.
15 Carat Ordinary (2)	Standard gold 17, pure copper
	4, pure silver 2, brass 1, dwts.
14 Carat Solder	Pure gold 14 dwts., pure silver
	5 dwts., pure copper 3 dwts.
	12 grs., pure zinc 1 dwt.
12 Carat, or No 3 (1)	12 grs. Pure gold 12, pure copper 6,
12 Carat, or 110 3 (1)	pure silver 5, brass 1, dwts.
12 Carat, or No 3 (2)	Standard gold 13, pure silver 6,
- , ,	pure copper 5, dwts.
Plumber's Solder	2 parts lead to 1 part tin.
Soft or Common Solder	50 parts lead and 50 parts tin.
Silver Solders:	Cilver 66 conner co vino to
10. I	Silver 66, copper 30, zinc 10, parts.
No. 2	Silver 6, copper 2, brass 1, parts.
No. 3	Silver 4, brass 3, parts.
No. 4	Silver 20, brass 10, zinc 5,
	copper 1, parts.
No. 5	Silver 4, brass 2, zinc 1, parts.
No. 6 Speculum Metal	Coin silver 9, zinc 1, parts.
Sterro Metal	Tin 33, copper 67, parts. Copper 55 to 70, zinc 34 to 44,
	iron I to 2, tin I to 2, per cent.
Tiersagent	Aluminium 66.5, silver 33.5, per
	cent.
Tutenag	Copper 45.7, nickel 17.4, zinc
Type Wetal (r)	36.9, per cent.
Type Metal (1) Type Metal (2)	Antimony 25, lead 75, parts. Antimony 18, lead 70, tin 10,
13 po metar (2)	copper 2, parts.
Type Metal (3)	Antimony 1, lead 8, tin 1, parts.
Victoria Metal	Copper, nickel, zinc, with copper
	in excess.
Von Eckhart Alloy	Copper 11.71, silver 3.53, plat
	inum 2·40.

TABLE OF PHYSICAL CONSTANTS OF THE MORE IMPORTANT METALS.

Name of Metal.	Symbol.	Atomic Weight.	Specific Gravity.	Specific Heat.	Melting- Point (° C.).
Aluminium	Al	27.10	2.56	0.218	657
Antimony	Sb	120-20	6.41	0.021	632
Bismuth	Bi	. 208•00	9.80	0.031	266
Cadmium	Cd	112.40	8.60	0.057	322
Copper	Cu	63.57	8.93	0.098	1,084
Gold	Au	197•20	19.30	0.032	1,064
Iridium	Ir_	193•10	22.42	0.033	1,950
Iron	Fe	55.85	7.86	0.110	1,505
Lead	Pb	207.10	11.37	0.031	327
Manganese	Mn	54.93	7.50	0.120	1,207
Mercury	Hg	200.00	13.59	0.032	-39
Nickel	Ni	58•70	8·8o	0.108	1,427
Palladium	Pd	106.70	11.20	0.059	1,535
Platinum	Pt	195.0	21.50	0.033	1,745
Silver	Ag	107.88	10.53	0.056	962
Tin	Sn	119.00	7.30	0.056	232
Tungsten	W	184.00	19.10	0.033	3,100
Zinc	Zn	65.37	7.12	0.094	418

Note.—The figures given above are those on which many authorities agree, and are only to be taken as approximately correct, as no two pieces of metal would yield the same result.

TABLE OF CONDUCTING POWERS OF METALS FOR HEAT AND ELECTRICITY.

Metal.	 Thermal Conductivity (Ag=100).	Electrical Conductivity (Hg at 0°=1).
Aluminium	 31•33	31•726
Antimony	 4.03	2.053
Bismuth	 i.8 ,	0.800
Cadmium	 20.06	13.95
Copper	 73•6	55.86
Gold	 53.2	43.84
Iron	 11.0	8.340
Lead	 8.5	4.818
Mercury	 1.3	i.000
Nickel	 <u> </u>	7*374
Palladium	 	6.910
Platinum]	 8•4	8.257
Silver	 100.0	[57.226
Tin	 15.2	8.237
Zinc	 28.1	16.92

# TABLE OF CORRESPONDING TEMPERATURES ON THE SCALES OF CENTIGRADE AND FAHRENHEIT THERMOMETERS.

Degrees Cent.	Degrees Fahr.	Degrees Cent.	Degrees Fahr.	Degrees Cent.	Degrees Fahr.
100	212.0	66	150.8	32	89•6
99	210.5	65	149.0	31	87.8
98	208.4	64	147.2	30	86.0
97	206.6	63	145.4	29	84.2
96	204.8	62	143.6	28	82.4
95	203.0	61	141.8	27	80.6
95	201.2	60	140.0	26	78.8
	199.4		138.2	25	77.0
93		59 58	136.4	25 24	
92	197.6				75*2
	195.8	57	134.6	23	73°4 71°6
90	194.0	56	132.8	21	69.8
88	192.2	55	131.0		68.0
87	190•4 188•6	54	129.2	20	66.2
86	186.8	53	127.4	19 18	
		52	125.6		64•4
85	185.0	51	123.8	17	62.6
84	183.2	50	122.0	16	60.8
83	181.4	49	120.2	15	59.0
82	179.6	48	118.4	14	57*2
81	177.8	47	116.6	13	55'4
80	176.0	46	114.8	12	53.6
79	174.2	45	113.0	II	51.8
78	172.4	44	111.2	10	50 <b>·0</b>
77	170.6	43	109•4	9 8	48.2
76	168.8	42	107•6		46•4
75	167.0	4I	105.8	7 6	44.6
74	165.2	40	104.0		42.8
73	163.4	39	102.2	5	41.0
72	161.6	38	100.4	4	39.2
71	159.8	37	98•6	4 3	37.4
70	158.0.	36	96•8	2	35.6
69	156.2	35	95.0	I	33.8
68	154.4	34	93.2	0	32.0
67	152.6	33	91.4		
		l		·	1

# CONVERSION OF CENTIGRADE AND FAHRENHEIT DEGREES.

These scales are convertible by the following rules:

$$\mathbf{i} \circ \mathbf{C} = \frac{9}{5} \times \mathbf{i} \circ \mathbf{F}.$$
  
 $\mathbf{i} \circ \mathbf{F} = \frac{5}{9} \times \mathbf{i} \circ \mathbf{C}.$ 

Therefore, to convert Centigrade into Fahrenheit, multiply by 9, divide by 5, and add 32.

To convert Fahrenheit into Centigrade, subtract 32, multiply

by 5, and divide by 9.

I litre ..

$$n^{\circ} C = \left(\frac{9}{5} n^{\circ} - 32^{\circ}\right) F.$$
  
 $n^{\circ} F = \frac{5}{9} (n^{\circ} - 32^{\circ}) C.$ 

## WEIGHTS AND MEASURES.

#### TROY WEIGHT.

```
4 grains . . . I carat (c)
6 carats, or 24 grains . I pennyweight (dwt.).
20 pennyweights . I ounce (oz.).
12 ounces . . . I pound (lb.).
25 pounds . . I quarter (qt.).
100 pounds . . I hundredweight (cwt.).
20 hundredweights . I ton of gold or silver.
```

#### IMPERIAL OR AVOIRDUPOIS WEIGHT.

```
16 drachms .. . . I ounce (oz.).
16 ounces .. . I pound (lb.).
14 pounds .. . I stone (st.).
28 pounds .. . I quarter (qt.).
4 quarters, or 112 pounds I hundredweight (cwt.).
20 hundredweights .. I ton.
```

# METRIC EQUIVALENTS IN ENGLISH MEASURES.

```
1 millimetre .. .. = 0.03937 inch.
r centimetre ...
                                       .. = 0.39371 inch.
I decimetre ..
                                    .. = 3.93718 inches.
ı metre
                                    \dots = 39.37 inches, or 1.093 yards.
                         . .
I inch .. .. = 2.539 centimetres.

I foot .. .. = 3.0479 decimetres.

L cubic centimetre .. = 0.061 cubic inch, or 0.00176 pint.
I litre, or 1,000 c.c. \dots = 61.027 cubic inches, or 1.76 pints.
Intre, or 1,000 c.c. ... = 61-027 cubic inches, or 1.7

I cubic inch ... = 16-38 cubic centimetres,

I gallon ... = 4-543 litres,

I milligramme ... = 0-0154 grain,

I decigramme ... = 1-5432 grains,

I gramme ... = 15-432 grains,

I kilogramme ... = 15-432 grains,

I kilogramme ... = 15-432 grains,

I grain ... = 0-0647 gramme,

I gramme ... = 1 gramme ... = 1 gramme ... = 1 gramme ...
I grain.. .. = 0.0647 gramme.
I gramme .. = I cubic centimetre.
I cubic centimetre .. = 17 minims.
 I ounce troy (480 grains) = 31·1034 grammes.
     ounce
                      avoirdupois
(437.5 grains) .. = 28.30625 grammes.
1 kilogramme .. = 2.2046 pounds.
                                    .. = 0.453 kilogramm
1 pound ....
```

.. .. = 0.220 gallon.

#### TROY WEIGHT.

(Used only for Gold, Silver, and Platinum.)

```
24 grains .. . make I pennyweight (dwt.). 20 pennyweights .. ,, I ounce (oz. tr.).
```

Apothecaries, in compounding medicines, subdivided a troy ounce into 8 drachms, a drachm into 3 scruples, and a scruple into 20 grains.

The pound troy, containing 12 ounces, is not used now.

#### AVOIRDUPOIS WEIGHT.

```
      16 drachms
      ...
      ...
      make I ounce (oz.).

      16 ounces
      ...
      ...
      ,...
      I pound (lb.).

      28 pounds
      ...
      ...
      ,...
      I quarter (qr.).

      4 quarters, or 112 pounds
      ...
      ,...
      I hundredweight (cwt.).

      20 hundredweights
      ...
      ,...
      I ounce avoirdupois.

      480 grains
      ...
      ,...
      I ounce troy.

      7,000 grains
      ...
      ,...
      I pound avoirdupois.
```

#### METRIC MEASURES.

(The most important measures are in heavier type.)

#### MEASURES OF LENGTH.

```
10 millimetres (mm.) ... = 1 centimetre (cm.).
10 centimetres ... = 1 decimetre (dm.).
10 decimetres ... = 1 metre (m.).
10 metres ... = 1 decametre (Dm.).
10 decametres ... = 1 hectometre(Hm.).
10 hectometres ... = 1 kilometre (Km.).
```

#### MEASURES OF AREA.

```
... is q. centimetre (sq. cm.).

100 sq. centimetres ... ... = 1 sq. centimetre (sq. cm.).

100 sq. decimetres ... ... = 1 sq. decimetre (sq. dm.).

100 sq. metres ... ... = 1 sq. metre (sq. m.) = 1 centiare.

100 sq. decametres ... = 1 sq. decametre (sq. Dm.) = 1 are.

100 sq. decametres ... = 1 sq. hectometre (sq. Hm.) = 1 hectare.

100 sq. hectometres ... = 1 sq. kilometre (sq. Km.).
```

#### MEASURES OF VOLUME.

```
1,000 cubic millimetres (c.mm.) = 1 cubic centimetre (c.cm.).
1,000 cubic centimetres .. = 1 cubic decimetre (c.dm.).
1,000 cubic decimetres .. = 1 cubic metre (cm.). = 1 stere.
```

#### MEASURES OF CAPACITY.

```
no centilitres (cl.)

no decilitres

``

### NOMENCLATURE OF ELECTRICAL UNITS.\*

A unit of resistance is termed an "ohm," and is equal to that offered by 1.0486 metres length of mercury of 1 square millimetre section at 0° C.

A unit of electro-motive force (E.M.F.) is called a "volt."

A unit of strength of current is termed an "ampère," and is the strength produced by an E.M.F. of I volt in a circuit having the resistance of an ohm.

<sup>\*</sup> Gore's "Electro-Metallurgy," p. 387.

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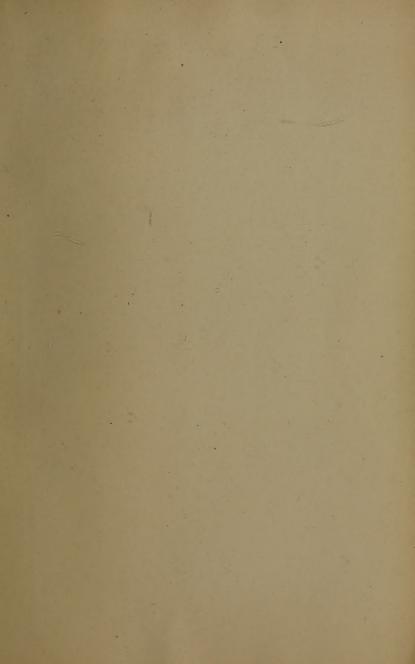
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